MASTER

NUCLEAR CHEMISTRY RESEARCH

DO NOT PHOTOSTAT

ANNUAL PROGRESS REPORT
CONTRACT AT-(40-1)-277
JANUARY 1, 1961

UNIVERSITY OF ARKANSAS
DEPARTMENT OF CHEMISTRY

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

ORO-367

UNIVERSITY OF ARKANSAS
Department of Chemistry
Fayetteville

NUCLEAR CHEMISTRY RESEARCH

Annual Progress Report
United States Atomic Energy Commission Contract
AT-(40-1)-277

January 1, 1961

Arthur Fry and R. W. Fink
(Joint Senior Investigators)

LEGAL NOTICE

This report was prepared as an account of Government sponsored work Neither the United States, nor the Commission, nor any person acting on behalf of the Commission

A Makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights, or

B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission, or employee of such contractor, to the extent that such employee or contractor of the Commission, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Commission, or his employment with such contractor.

TABLE OF CONTENTS

List of Appendices

I. D. M. Chittenden II, D. G. Gardner and R. W. Fink, A New Isotope of Manganese; Cross-Sections of the Iron Isotopes for 14.8 Mev Neutrons, submitted for publication, 1960. Preprint.

II. R. W. Fink, G. Andersson and J. Kantele, Nuclear Spectroscopy of Mass Separated Neutron-Deficient Tellurium Isotopes, Arkiv for Fysik, submitted for publication, 1960. Abstract and proposed decay schemes.

III. A. Poularikas, S. Umemoto, E. Bramlitt and D. G. Gardner, Some Additional (n,He^3) Reactions Induced by 14.8 Mev Neutrons, submitted for publication, 1960. Preprint.

IV. I. Kumabe, A. D. Poularikas, I. L. Preiss, D. G. Gardner and R. W. Fink, (n,He^3) Reactions of Medium Weight Nuclei Induced by 14.8-Mev Neutrons, Phys. Rev. 117, 1568 (1960). Reprint.

V. D. G. Gardner and L. M. Epstein, Protection Against Radiation Damage in Polymethylmethacrylate by High Energy Electrons and by Ultraviolet Light, J. Chem. Phys., accepted for publication, 1960. Preprint.

VI. I. L. Preiss and R. W. Fink, New Isotopes of Cobalt; Activation Cross-sections of Nickel, Cobalt and Zinc for 14.8 Mev Neutrons, Nuclear Phys. 15, 326 (1960). Reprint.

VII. R. G. Wille and R. W. Fink, Activation Cross-Sections for 14.8-Mev Neutrons and Some New Radioactive Nuclides in the Rare Earth Region, Phys. Rev. 118, 242 (1960). Reprint.

VIII. A. Poularikas, J. Cunningham, W. McMillan, J. McMillan and R. W. Fink, New Isomers of Scandium-50 and Indium-120; Gamma-rays in Lutecium-178 Decay, J. Inorg. and Nuclear Chem. 15, 196 (1960). Reprint.

IX. I. Kumabe and R. W. Fink, The Angular and Energy Distribution of Protons from Ni^{58} Reactions Induced by 14.8 Mev Neutrons, Nuclear Phys. 15, 316 (1960). Reprint.

X. H. M. Schwartz, Ritz-Hylleraas Solutions of the Ground State of Two-Electron Atoms Involving Fractional Powers, Phys. Rev. 120, 483 (1960). Reprint.

XI. C. T. Davis and A. Fry, Oxygen Function Rearrangement in 3,3-Dimethylbutan-2-one-[2-^{14}C], Chem. & Ind. (London), 227 (1960). Reprint.

XII. A. Fry, M. Eberhardt and I. Ookuni, Acid-Catalyzed Rearrangement of Diethyl Ketone and Diisopropyl Ketone, J. Org. Chem., 25, 1252 (1960). Reprint.

XIII. D. Jeffrey, The Kinetics of Oxygen Exchange of Substituted Benzyl Alcohols as a Function of Acidity, Ph.D. Dissertation Abstract, University of Arkansas, 1961.

XIV. J. Hill, Chlorine Isotope Effects in the Reactions of Benzyl and Substituted Benzyl Chlorides with Various Nucleophiles, Ph.D. Dissertation Abstract, University of Arkansas, 1961.

PART I. RESULTS OF RESEARCH IN NUCLEAR CHEMISTRY AND PHYSICS, THEORETICAL PHYSICS AND ORGANIC ISOTOPE CHEMISTRY

A. CURRENT INVESTIGATIONS IN NUCLEAR CHEMISTRY AND PHYSICS

1. Absolute Activation Cross-sections for 14.8 Mev Neutrons; Identification of New Nuclear Species.

This part of the research program in nuclear chemistry is concerned with the measurement of cross-sections of the more familiar fast neutron-induced reactions. For the most part the work has been concerned with (n,p), (n,2n) and (n,α) reactions. As will be further explained in section I-A-5, this type of work will be continued in order to try to clear up the serious discrepancies that exist in the literature for almost all cross-sections that have been measured more than once. Better cross-section data will have to be obtained before much more work can be done in the theoretical study of these reactions. However in the forthcoming year we plan to extend the scope of this research program to cover, in addition, nuclear decay scheme studies and the study of the energy and angular distributions of the emitted particles by means other than nuclear emulsion studies. The nuclear emulsion program described in the previous annual report has now been terminated.

(a) The study of the 14.8 Mev neutron-induced reactions on the isotopes of iron has been completed. The results from the bombardment of samples enriched to about 97% in the isotope Fe^{54} are:

$Fe^{54}(n,t)Mn^{52m}$: $\sigma = 0.6 \pm 0.1$ mb
$Fe^{54}(n,2n)Fe^{53}$: $\sigma = 7.9 \pm 0.8$ mb
$Fe^{54}(n,\alpha)Cr^{51}$: $\sigma = 270 \pm 135$ mb

An activity with a half-life of about 5 days appeared in the manganese fraction. This is thought to be Mn^{52g} resulting from the (n,t) reaction, but the activity was so low that this conclusion has not been confirmed. This work, which constitutes a portion of the M.S. thesis of Mr. D. M. Chittenden, has been submitted for publication and a preprint appears as Appendix I.

An iron sample enriched to 78% in the isotope Fe^{58} was bombarded in an attempt to find the unknown isotope Cr^{56} produced by an (n,He^3) reaction. While the chemically separated chromium fraction contained no activity, the (n,He^3) reaction cannot be definitely excluded since the half-life of Cr^{56} might be relatively long.

Bombardments of natural chromium (83% Cr^{52}) and samples enriched in the isotopes Cr^{50} and Cr^{53} yielded the following data:

$Cr^{50}(n,2n)Cr^{49}$: $\sigma = 18.8 \pm 1.9$ mb
$Cr^{52}(n,p)V^{52}$: $\sigma = 82.7 \pm 9.0$ mb
$Cr^{53}(n,p)V^{53}$: $\sigma = 37.3 \pm 3.7$ mb

Further work on the reactions of the chromium isotopes is now underway.

(D. M. Chittenden and D. G. Gardner)

(b) In a continuation of the study of neutron reactions around the closed neutron shell at N = 50 (as reported in the previous annual progress report) the following additional cross-sections were measured:

$Sr^{88}(n,p)Rb^{88}$: $\sigma = 11.2$ mb
$Sr^{88}(n,2n)Sr^{87m}$: $\sigma = 43.6$ mb
$Zr^{94}(n,p)Y^{94}$: $\sigma = 6.88$ mb
$Zr^{94}(n,\alpha)Sr^{91}$: $\sigma = 5.32$ mb
$Zr^{92}(n,p)Y^{92}$: $\sigma = 22.5$ mb
$Zr^{96}(n,\alpha)Sr^{93}$: $\sigma = 9.6$ mb
$Zr^{91}(n,p)Y^{91}$: $\sigma = 171.4$ mb

One bombardment was made on Tc^{99}, yielding a 13.5 hr unassigned activity and several longer-lived activities. Chemical separations will be required to obtain cross-section values due to the high initial activity of the Tc^{99} sample.

In the study of the nuclear reactions of niobium an activity was observed which indicated the possibility of an (n,2p) type of reaction:

$$Nb^{93}(n,2p)Y^{92},\ 3.1\ \text{hr},\ 0.24\ \text{mb}.$$

Since no such reaction has been detected at this energy (although several authors have suggested its possibility), interest was shifted to a search for other examples. Nuclides chosen for study were in most cases the heaviest isotopes of elements, or monoisotopic elements, so as to prevent the desired product from being produced in any manner except by the (n,2p) reaction. Since the yield was expected to be only a few tenths of a millibarn, it was expected that chemical separations would be required in most cases. The product of an (n,2p) reaction will be of the same Z as that of an (n,α) reaction so that an internal standard is available whenever the (n,α) cross-section is known.

Nuclides which definitely showed no (n,2p) reaction were:

$$Y^{89},\ V^{51},\ Sc^{45},\ Cs^{133},\ Tb^{159}.$$

No cross-section upper limits were placed on these nuclides, but it is estimated that any reaction would have a σ less that 0.1 mb. Other nuclides which were studied but for which the (n,2p) reaction has not been ruled out definitely are:

$$As^{75},\ Pr^{141},\ C^{12}\ \ Re^{187}\ \ K^{41}.$$

In most cases the time of chemical separation was too long to detect the desired product. Bombardment of As^{75} followed by solvent extraction of gallium produced an activity of about 8 min. half-life when counted in a well counter. This could possibly have been Ga^{74}. When the sample was precipitated as the oxinate and counted, too few counts were available for a definite conclusion. In the bombardment of rhenium, an activity of about 10 min half-life was found suggesting the possibility that Ta^{186} was produced. Difficulties were incountered in that the rhenium reacts with the paper bag used for a container. No chemistry was performed. The C^{12} gave an activity of about 7 sec half-life. Seven different sources of carbon were employed and all gave the same short-lived activity. Extensive tests were made to remove oxygen and still the activity was present. B^{11} is reported to have a half-life of 14 sec and so if this is not the product of the carbon bombardments then perhaps a new isomeric state has been observed. Further investigation of this nuclide is planned.

Since no other examples of the (n,2p) reaction were definitely shown to exist, a more careful investigation of the niobium was performed. Samples of both niobium pentoxide and potassium hexa-niobate, of purity greater than 99%, were treated chemically, after neutron irradiation, to separate zirconium and yttrium. The 3.1 hr (as well as 64 hr) activity was found to follow only the yttrium fraction. The ratio of the 3.1 hr and the Y^{90} activities in three samples was $2.70 \pm 0.02 \times 10^{-2}$. One sample of the yttrium fraction was counted with a NaI crystal set to count gammas of energy between 0.15 and 0.25 Mev. A straight line was obtained with slope corresponding to 3.1 hr. It was followed for about 22 hrs (7 half-lives). The literature (1) reports a $t_{1/2}$ for Y^{92} of 3.6 ± 0.6 hr.

The gamma spectrum of the yttrium fraction was also studied. By using an oscilloscope and camera attached to a linear amplifier it was possible to detect two gammas of energy 0.21 and 0.47 Mev. Similar gamma rays have been reported (1) for Y^{92}; however, the higher energy gammas were not observed. Using the same camera arrangement with a beta detector, it was impossible to locate any high energy betas. The literature (1) reports a strong beta ray of energy 3.6 Mev. Using a single channel analyzer and the hollow well beta scintillator, no

---

(1) D. G. Gardner, AECU-3514 (1957).

better results were obtained. It is planned to use the newly purchased multichannel analyzer to get more complete spectra. Until this is done it can not be said that the (n,2p) reaction definitely occurs.

While looking for the (n,2p) reaction, the following cross-sections were determined:

$Tb^{159}(n,p)Gd^{159}$: $\sigma = 2.16$ mb
$Gd^{158}(n,\gamma)Gd^{159}$: $\sigma = 3.41$ mb
$As^{75}(n,\alpha)Ga^{72}$: $\sigma = 4.59$ mb

In the bombardment of As^{75} it was observed that no (n,He^{3}) reaction occured as has been reported (2). The gallium fraction showed a straight line of slope corresponding to a 14.1 hr half-life only.

(E. Bramlitt and D. G. Gardner)

(c) Utilizing the newly installed pneumatic transport system a number of preliminary cross-section values were obtained for some relatively short-lived activities.

$B^{11}(n,p)Be^{11}$: $\sigma \approx 3.3$ mb
$O^{16}(n,p)N^{16}$: $\sigma = 39 \pm 4$ mb
$F^{19}(n,p)O^{19}$: $\sigma \approx 17$ mb
$F^{19}(n,\alpha)N^{16}$: $\sigma \approx 58$ mb
$Al^{27}(n,p)Mg^{27}$: $\sigma = 86 \pm 8$ mb

Assuming (3) the cross-section ratio $\frac{\sigma B^{11}(n,\alpha)}{\sigma B^{11}(n,p)} = 10$ the following cross-section was obtained:

$B^{11}(n,\alpha)Li^{8}$: $\sigma \approx 33$ mb

---

(2) I. Kumabe, et. al., Phys. Rev. 117, 1568 (1960).

(3) N. J. Nurmia and R. W. Fink, Phys. Rev. Letters 1, 226 (1958).

The $B^{11}(n,p)Be^{11}$ cross-section has not been reported previously.

(J. Kantele and D. G. Gardner)

(d) R. G. Wille (4) has observed a 9 ± 1 min activity produced during the bombardment of erbium. In an attempt to identify this new activity samples of Tm_2O_3 have been bombarded. These samples were 99.99% pure Tm_2O_3. Again a 9 ± 1 min activity was observed. It is thought that it arises from the reaction $Tm^{169}(n,p)Er^{169}$, although the $Tm^{169}(n,2n)Tm^{168}$ reaction is also a possibility. Either reaction requires that a new isomeric state be postulated. The cross-section appears to be of the order of 5-10 mb which supports the (n,p) possibility. Work on this isotope is continuing.

(A. Poularikas and D. G. Gardner)

(e) As part of an undergraduate research participation program during the summer of 1960 a study of the neutron reactions on Mn^{55} was begun. The following results were obtained:

$$Mn^{55}(n,\alpha)V^{52} : \sigma = 11.8 \pm 0.7 \text{ mb}$$
$$Mn^{55}(n,2n)Mn^{54} : \sigma < 1 \text{ mb}$$

In both cases chemical separations were employed. No trace of the previously reported 2 min isomeric state of Mn^{54} was found (5).

(J. Nix, D. Chittenden and D. G. Gardner)

---

(4) R. G. Wille, Ph.D. thesis, University of Arkansas, 1959.

(5) A. Caldwell and S. Stoddart, Phys. Rev. 81, 660A (1951).

2. Nuclear Spectroscopy of Mass Separated Neutron-Deficient Tellurium Isotopes.

This problem was carried out at the Gustaf Werner Institute for Nuclear Chemistry, Uppsala, Sweden, during 1959/60 and is now completed. The abstract and proposed decay schemes of Te^{116}, Te^{117}, Te^{118}, and Te^{119} are included as Appendix II. The full paper by Fink, Andersson and Kantele is being communicated to the Swedish Physics Journal, Arkiv for Fysik for publication.

(R. W. Fink)

3. The (n,He^3) Reaction.

A further investigation of the (n,He^3) reaction reported by Kumabe, et al (2) and described in the previous annual report is almost completed. The following new cross-sections have been measured:

$Cu^{65}(n,He^3)Co^{63}$: σ = 1-3 mb
$Zr^{94}(n,He^3)Sr^{92}$: σ = 0.9-1.0 mb
$Nd^{148}(n,He^3)Ce^{146}$: σ = 0.6-0.8 mb
$K^{41}(n,He^3)Cl^{39}$: $\sigma < 0.2$ mb (not observed)
$Mg^{26}(n,He^3)Ne^{24}$: $\sigma < 0.5$ mb (not observed)

In the above work chemical separations were performed for potassium, zirconium and neodymium. In the case of Zr^{94} it was assumed that the $Zr^{90}(n,\alpha)Sr^{87}$ cross-section was 10 mb and that the gamma ray efficiency of the counter employed was 3%.

As was mentioned previously in section I-A-1-b, the previously reported (2) (n,He^3) cross-section for As^{95} is in error. After chemical separation the gallium fraction showed no 5.1 hr Ga^{73} to be present. The new cross-section value is:

$As^{75}(n,He^3)Ga^{73}$: $\sigma < 0.5$ mb (not observed).

A note covering this work has been submitted to the Physical Review and a preprint appears as Appendix III. A reprint of the first (n,He^3) paper appears as Appendix IV.

(A. Poularikas, S. Umemoto, E. Bramlitt
and D. G. Gardner)

4. The (n,t) Reaction.

In one view of the mechanism of low energy nuclear reactions (6) surface interactions play an important part. Involved in these interactions are clusters in the nuclear surface. Alpha-particle clusters are dominant, but He^3, t, and d clusters are also supposed to exist to a certain extent. One possible mechanism for the (n,He^3) reaction would be a direction interaction of the neutron with a He^3 cluster. Hence one would also expect to find (n,t) reactions. As was mentioned in section I-A-1-a the Fe^{54}(n,t)Mn^{52m} cross-section has already been measured. Unfortunately there are relatively few cases where the daughter product is not stable or long-lived. It was therefore decided to count the tritium to determine (n,t) cross-sections. The general procedure will be to bombard a target, place it in a vacuum system, heat the target with an induction heater, and sweep the outgassed tritium into a gas proportional counter. This counter will be surrounded by an anticoincidence counter to lower the background counting rate. The gas counter has been built and is now under test, and the vacuum system is under construction.

Using the technique described above one is not dependent on a radioactive daughter product, and so almost all of the stable isotopes may be studied. Measureable cross-sections are expected for a large number of isotopes since the (n,t) reaction is exoergic in most cases.

(A. Poularikas and D. G. Gardner)

---

(6) D. H. Wilkinson, Phil. Mag. 4, 215 (1959).

5. Neutron Cross-Section Trends Around 14 Mev.

A literature survey has been made of the cross-sections reported for neutron-induced reactions around 14 Mev. The survey has been carried up to 1958 so far except for the (n,p) reaction case where the survey is now up to date. It was felt that such a survey would be of value in the theoretical study of these reactions. The first result of this survey was to indicate the exceptionally poor quality of most cross-section data. For reactions whose cross-sections have been measured more than once there is commonly a factor of 2 spread in the results. In quite a few cases there is close to a factor of 10 spread. The (n,p) reaction on Al^{27} is a typical case. The following cross-sections in millibarns have been found in the literature: 52 ± 9, 79 ± 6, 55 ± 10, 87 ± 7, 115 ± 10, 53 ± 5, ~ 70, 52.4 ± 10, and 86 ± 8. The errors attached to these values appear to have little meaning. A few examples of more extreme cases are the following (n,p) values (again in millibarns): F^{19}(135 ± 50 and 18 ± 4), Ti^{49}(29 ± 5 and 97 ± 16), Ni^{61}(22 ± 2 and 181 ± 27) and As^{75}(11.8 ± 2 and 115 ± 15). Before theoretical calculations can be tested better experimental data must be available. An attempt is being made to detect trends in these cross-section data in the hope that this will enable the "best" cross-sections to be chosen from the literature. Some very interesting results have already appeared. In Figure 1 and Figure 2 we show the reported (n,p) cross-sections around 14 Mev for the elements from potassium (Z = 19) to copper (Z = 29). The solid lines were calculated using the following set of empirical equations:

$$\sigma(Z,A) = 0.0222A \exp\left[0.0867A - 0.035\,(Z - 22)\right] \qquad (1)$$

$$A = 2Z + 4 \qquad (2)$$

$$\sigma(A \pm 1) = \sigma(A)2^{\mp 1} \qquad (3)$$

The first equation allows one to calculate the cross-section for one

Caption for Figure 1

Literature values for the (n,p) cross-sections around 14 Mev for the elements potassium through chromium. The * points were calculated from cross-section ratios from references where absolute values were not given. The lower values were obtained by assuming the upper value and then multiplying by the stated ratio. The * points are only used to check the slope of the calculated cross-section curves given by the solid straight lines. These curves were calculated using the equation given in the text.

Caption for Figure 2

Literature values for the (n,p) cross-sections around 14 Mev for the elements vanadium through copper. The solid lines are the calculated cross-sections using the equations given in the text.

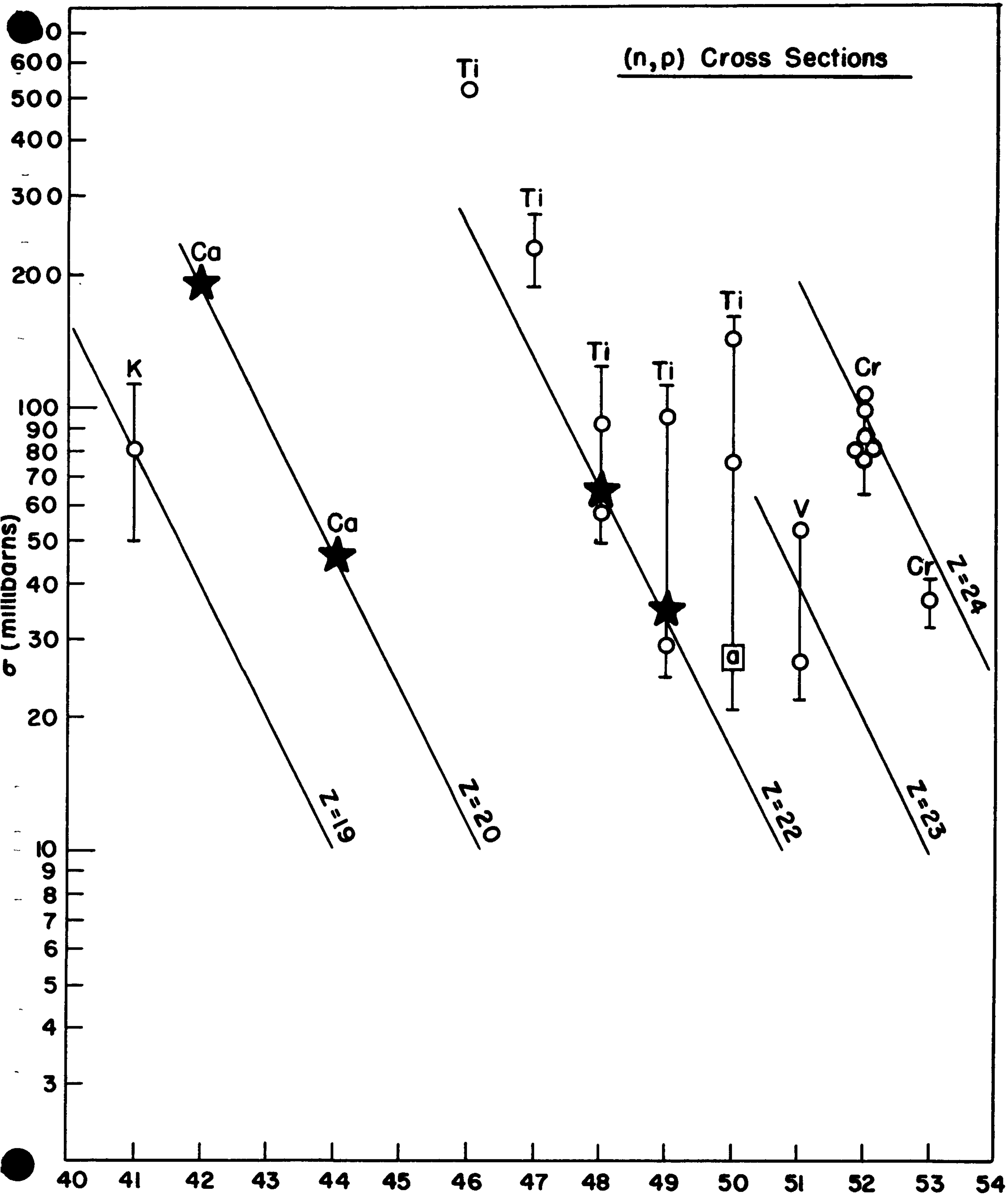


Figure 1. Mass Number A

427 18

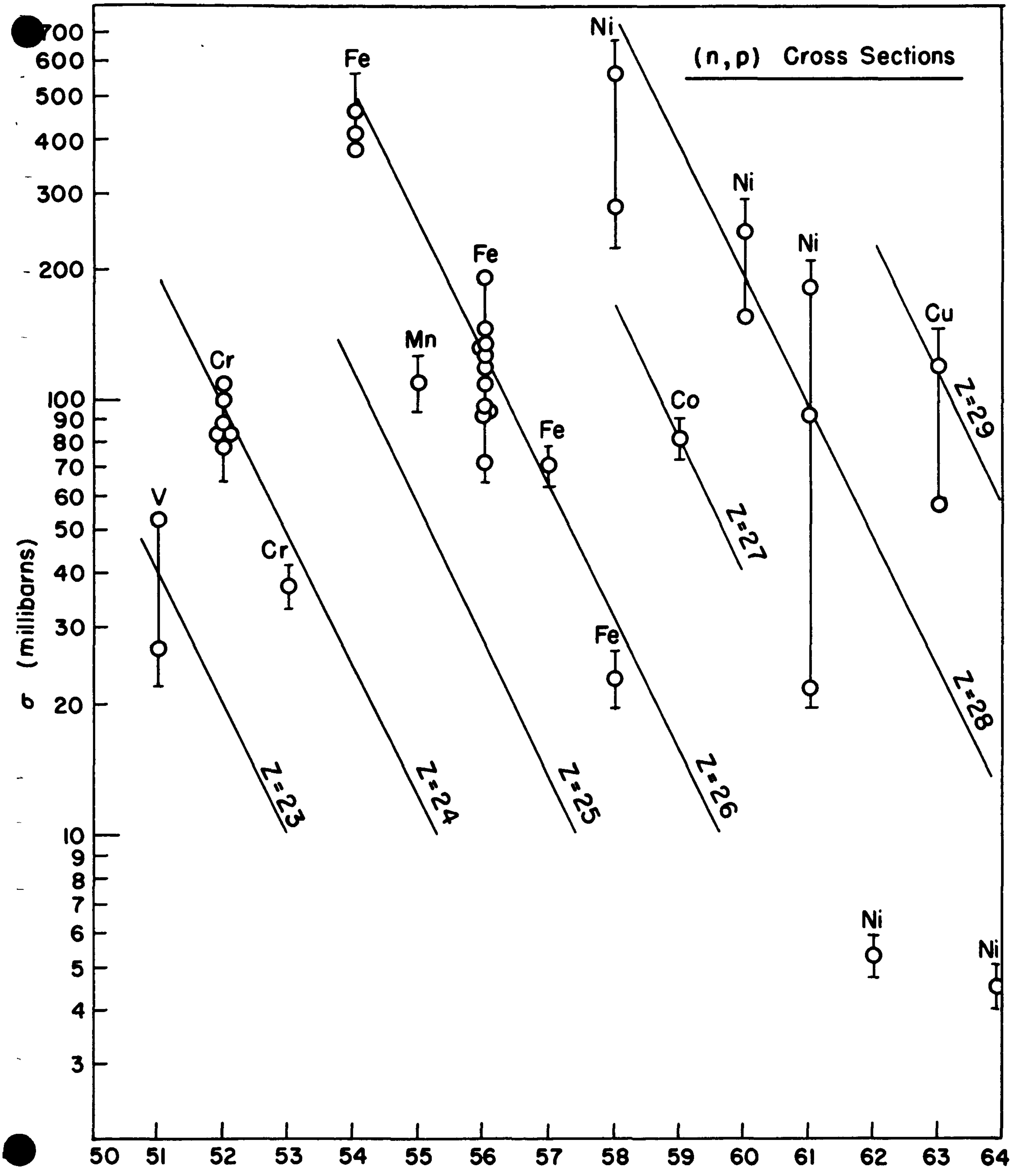


Figure 2. Mass Number A

427 17

isotope for each element. For example, for the element cobalt (Z = 27) one calculates the cross-section for the isotope with mass A = 2Z + 4 = 58. Then, by use of the recursion formula (Equation 3) the cross-sections of all of the other isotopes may be calculated.

$$\sigma(\mathrm{Co}^{59}) = \frac{\sigma(\mathrm{Co}^{58})}{2} = \frac{160}{2} = 80 \text{ mb.}$$

It can be seen that this empirical calculation yields curves that fit the experimental values surprisingly well. The same equations can be applied to all of the elements from oxygen (Z = 8) to arsenic (Z = 33) with good success.

Why such a simple formulation should fit so many elements is not clear. The factor of 2 change in cross-section is the same result that Levkovskii found (7), but the only other factor that enters into the equations is just the atomic number of the element. Closed neutron shells produce no special deviation, although the closed proton shell at Z = 28 shows some effect in the expected direction. The Q value seems to enter only through the recursion formula. No effect relating to odd or even numbers of protons or neutrons is seen. The shape of the excitation function and the threshhold value seem unimportant, although 14 Mev certainly does not fall on a plateau in the excitation function in most of the known cases. The total nonelastic cross-section does not appear anywhere. While the exact form of Equation 1 is probably not significant, it is of theoretical interest that so simple a formulation could be found. This, together with the Levkovskii trend, should come out of any theoretical treatment of fast neutron-induced reactions.

While the (n,p) cross-sections always seem to follow the Levkovskii trends, this is not always the case for other neutron reactions.

---

(7) V. N. Levkovskii, Sov. Phys. JETP 6, 1174 (1958); 4, 291 (1957).

For example, the (n,α) cross-sections for Cd^{112}, Cd^{113} and Cd^{114} are given as 1.35 mb, 6.2 mb and 0.51 mb. These values are consistent with the Q values of 2.95 Mev, 4.7 Mev and 1.56 Mev however.

In general the (n,p) cross-sections tend to follow the Q values, particularly for reactions leading to an odd-even or an even-odd daughter. Both the Q values and the cross-sections plotted against mass number tend to peak in the mass range of 40-60. Similar plots for the (n,α) reaction show no such peak. Cross-section plots for the (n,2n) reaction show cross-sections in the range of 10-100 mb up to a mass number around 55, then between masses 55 and 70 the cross-sections increase to around 1000 mb. For heavier masses the cross-sections fluctuate between 700 and 2000 mb.

The study of similar cross-section trends is continuing.

(D. G. Gardner and A. Poularikas)

6. 14 Mev Neutron Induced Fission.

It has been reported in the last year's Annual Progress Report that the yields for U^{238} 14 Mev fission at mass numbers 89, 90, 91, 92, 131, 132, 133, 134, 135, 139, 140 and 141 will be measured during the current contract year. A sample of depleted uranium (isotopic composition; 99.989 % U^{238} and 0.011 % U^{235}), which was made available to us by Dr. H. M. Roth of Oak Ridge, was exhaustively purified to remove the chemical impurities, and was used for the experiments. The values of cumulative fission yields obtained so far are: Sr^{89}, 2.7%; Sr^{91}, 3.4%; I^{131}, 3.7%; I^{133}, 3.5%; Ba^{139}, 4.7% and Ba^{140}, 5.7% (tentative reference standard).

(K. M. Broom, Jr. and P. K. Kuroda)

7. Radiation Effects in Plastics.

(a) The problem of protecting plastics from damage by ionizing radiation and ultraviolet light has been studied by observing the protection afforded the plastic by small amounts of such additives as pyrene, p-terphenyl, benzene, and lead stearate. The results have been analyzed in terms of a model involving energy transport by both excited and ionized states of the plastic. The solid state kinetics for a general system are proposed. The theoretical treatment is based on experimental data from 2 Mev electron irradiations and ultraviolet irradiations obtained while Dr. Gardner was employed by Westinghouse Electric Corporation. A paper based on this work has been accepted for publication by the Journal of Chemical Physics and a preprint appears as Appendix V.

(D. G. Gardner)

(b) The damage produced by fast neutron irradiations of commercial plastics is under study. Preliminary results for lucite give a G value of about 0.17 main chain scissions per 100 ev. This may be compared with a G value of 1.56 for lucite exposed to 2 Mev electrons. It would appear that the high density of excitation and ionization along the track of the recoil proton (which is doing most of the damage) quenches the exciton states or interferes with their diffusion from the damage area. Work on this project is continuing.

(D. G. Gardner)

(c) A study is underway to determine the relative ease of energy migration down polymer chains as opposed to energy migration from chain to chain. Copolymers of polymethylmethacrylate and α-methyl styrene are being prepared and will be irradiated with high energy electrons and with ultraviolet light. At the present time methods for preparing the copolymers and for determining quantitatively the amount of α-methyl styrene in the copolymer samples are being studied.

(C. F. Smith and D. G. Gardner)

(d) A study of the effect of radiation damage in lucite on the index of refraction of lucite is underway. Both soft x-rays and 2 Mev electrons will be used. So far it has been found that the index of refraction varies with the direction of the light path through the material. This may be due to density gradients in the material. If we choose an arbitrary direction and call it zero degrees, then rotating a 1 cm^2 X 0.3 cm thick typical sample counterclockwise the following readings were obtained:

Direction	Index of Refraction
0^o	1.49090
90^o	1.49127
180^o	1.49274
270^o	1.49310

Surprisingly enough, it was observed that these values did not change after the sample was heat treated in an oven at 90^oC for 72 hours.

(A. Poularikas and D. G. Gardner)

8. List of Reprints of Papers Published During the Past Year on Work Described in the Previous Annual Report.

(a) Appendix IV. I. Kumabe, A. D. Poularikas, I. L. Preiss, D. G. Gardner, and R. W. Fink, "(n,He^3) Reactions of Medium Weight Nuclei Induced by 14.8-Mev Neutrons," Phys. Rev. 117, 1568 (1960).

(b) Appendix VI. I. L. Preiss and R. W. Fink, "New Isotopes of Cobalt; Activation Cross-sections of Nickel, Cobalt, and Zinc for 14.8 Mev Neutrons," Nuclear Phys. 15, 326 (1960).

(c) Appendix VII. R. G. Wille and R. W. Fink, "Activation Cross Sections for 14.8-Mev Neutrons and Some New Radioactive Nuclides in the Rare Earth Region," Phys. Rev. 118, 242 (1960).

(d) Appendix VIII. A. Poularikas, J. Cunningham, W. McMillan, J. McMillan, and R. W. Fink, "New Isomers of Scandium-50 and Indium-120; Gamma-rays in Lutecium-178 Decay," J. Inorg. and Nuclear Chem. 13, 196 (1960).

(e) I. Kumabe and R. W. Fink, "The Angular and Energy Distribution of Protons from Ni^{58} Reactions Induced by 14.8-Mev Neutrons," Nuclear Phys. 15, 316 (1960).

B. THEORETICAL PHYSICS

1. Molecular Excitation in Beta Decay.

The work on molecular excitation resulting from the beta decay of a constituent atom has continued along the lines discussed in the last Annual Report. Principal attention was again directed to the problems relating to dissociation in the tritium molecule. The investigation of a semi-classical method of computing the rotational-vibrational dissociation probabilities has been completed with the development of a quantum-mechanical justification of this method. This derivation is based on an extension of Pillow's empirical method of distorting harmonic oscillator wave functions in the calculation of line intensities in band systems of diatomic molecules (8). It reduces to the WKB method under suitable restrictive conditions (9). These results are presented in the master's thesis of W. MacMillan.

The calculations relating to the electronic transition probabilities are still in progress. A recalculation has been made of the electronic wave function of the ground state of ionized helium hydride for the expansion employed by Toh (10). The coefficients of this expansion which have been computed differ significantly from the corresponding coefficients published by Toh (10).

---

(8) M. E. Pillow, Proc. Phys. Soc. A 64, 772 (1951).

(9) A related approximation procedure is also contained in a paper by S. C. Miller, Jr. and R. H. Good, Jr., Phys. Rev. 91, 174 (1953).

(10) S. Toh, Proc. Phys. Math Soc. Jap. 22, 119 (1940). The necessary matrix elements were kindly supplied by Dr. A. A. Evet.

The pertinent overlap integral employing the recalculated Toh function is now being evaluated.

When these calculations are completed the results should be helpful in the examination of the more involved cases of complex molecules and in the attempt to formulate some workable zero-order methods of estimating disruption probabilities of large radioactive molecules. Recent experimental findings in this field (11), as well as possible radiobiological applications, lend interest to such studies.

(H. Schwartz and W. MacMillan)

2. Wave Functions of the Ground State of the Helium Atom.

Further calculations in elucidation of some of the questions raised by previous work on this topic have continued. That phase of the work which is based solely on desk calculator computation has been completed, and the results are summarized in a paper published recently, a reprint of which is attached as Appendix X. This paper is a revision of the preprint attached to last year's Report, and in addition to the results contained in that preprint includes also the result of a later calculation on a 12-term wave function for Z = 8 which yields an energy which differs by only 0.00006% from the 210-term wave function of Pekeris (12).

In order to determine the behaviour of the fractional-power wave functions as the number of parameters is increased beyond 18, a

---

(11) S. Wexler, G. R. Anderson and L. A. Singer, J. Chem. Phys. 32, 417 (1960) and references therein.

(12) C. L. Pekeris, Phys. Rev. 112, 1649 (1958).

double-precision program was prepared for the IBM 650 computer. This program has been checked out satisfactorily and initial results have been obtained for functions with 24 terms.

(H. M. Schwartz, J. E. Scroggs and C. L. Davidson)

The primary motivation for the present study of ground state helium wave functions has been explained in last year's Report. In order to be able to draw meaningful conclusions from such a study, it is desirable to have adequate criteria of goodness of atomic wave functions. In this connection one requires the expectation values $< H^2 >$ of the square of the atomic Hamiltonian operator H in the corresponding states. At the same time, these values enter also in a useful method for determining lower energy bounds, which when applied to the ground state of the helium atom can provide improved limits of accuracy on the presently known best theoretical energy value. The evaluation of $<H^2>$ for our wave functions leads to lengthy numerical work. A double-precision program for the IBM-650 computer is in preparation.

(H. Schwartz and J. Gardner)

3. Nuclear Reaction Theory.

The preliminary program outlined in last year's report is in the process of being completed. It is planned to concentrate on the theory of the (n,He^3) and (n,T) reactions which are being investigated experimentally in this laboratory. Tentative conclusions concerning the main processes that are involved in these reactions were reached with the employment of crude quantum mechanical approximations. It is planned to continue this work using more accurate calculations.

(H. Schwartz)

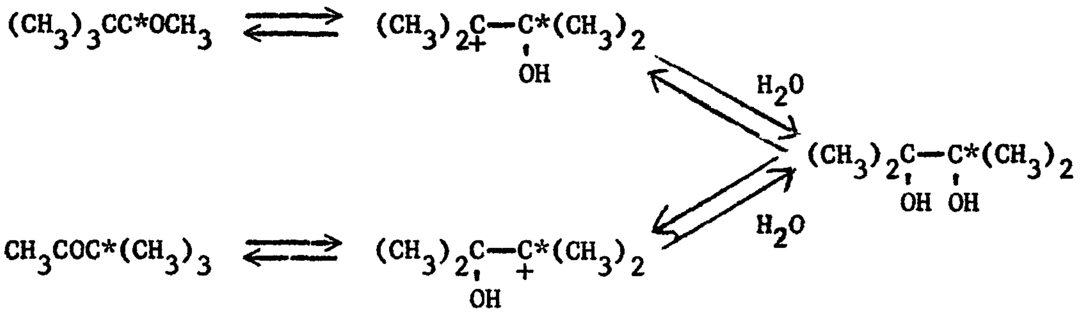
C. ORGANIC REACTION MECHANISM STUDIES

1. Mechanisms of Acid-Catalyzed Ketone Rearrangements.

(a) 3,3-Dimethyl-2-butanone-2-C^{14} and 3,3-Dimethyl-2-butanone-1-C^{14}. -- As reported in the last annual report, 3,3-dimethyl-2-butanone-2-C^{14} does not rearrange to 3,3-dimethyl-2-butanone-3-C^{14} under conditions where the carbon-14 in 3,3-dimethyl-2-butanone-1-C^{14} becomes equally distributed among all four methyl groups; however, this rearrangement does take place upon treatment of the ketone with perchloric acid for three hours at 100°. A communication reporting this work has been published in Chemistry and Industry, and a reprint of the paper appears as Appendix XI. Complete details are available in the M.S. thesis of Mr. Charles Davis, who will receive the M.S. degree in January, 1961.

(C. Davis and A. Fry)

The reasons for the difference in behavior of 3,3-dimethyl-2-butanone-2-C^{14} in 70% perchloric acid (where it rearranges to 3,3-dimethyl-2-butanone-3-C^{14}) and in conc. sulfuric acid (where it does not rearrange) are being investigated further. One possible explanation for this difference is that the greater amount of water present in the perchloric acid enables the symmetrical compound pinacol to be formed more readily, thus leading to rearrangement.



The rate of the rearrangement will be measured as a function of the water content of perchloric and sulfuric acid solutions. Also the rate of rearrangement of the isotopic isomer, 3,3-dimethyl-2-butanone-1-C^{14}, will be measured and compared to the rate for the carbonyl labelled compound to see if a common mechanism is involved. The synthetic methods previously used for preparation of the two labelled ketones gave very poor yields, and considerable effort has been made in the past few months to improve these yields, so far with little success.

(R. Barnes and A. Fry)

(b) Diethyl Ketone and Diisopropyl Ketone. -- A paper reporting the discovery that diethyl ketone rearranges to methyl propyl ketone and that diisopropyl ketone rearranges to 3,4-dimethyl-2-pentanone has been published in the Journal of Organic Chemistry, and a reprint appears as Appendix XII.

(A. Fry, M. Eberhardt and I. Ookuni)

(c) Rearrangement of Other Aliphatic Ketones. -- The surprising results on diethyl ketone mentioned above have led us to extend our investigation of the scope of the reaction to methyl ethyl ketone and methyl isopropyl ketone, compounds whose rearrangement can be studied only by the use of tracer techniques. Procedures have been worked out for the synthesis of both compounds labelled with carbon-14 in both the carbonyl and methyl groups. The preparations of 2-butanone-1-C^{14} and 2-butanone-2-C^{14} have just been completed, and the question of whether rearrangement takes place, and, if so, how fast, will be investigated in the immediate future.

(I. Ookuni and A. Fry)

(d) Rearrangements of Cyclic Ketones. -- The study of the scope of acid-catalyzed ketone rearrangements has been extended to cyclic compounds analogous to open chain compounds which are known to rearrange. No rearrangement was observed in any of the cases studied. In all cases the ketones were heated at 90° with 70% perchloric acid for times varying from 1 to 4 hours. The reaction mixtures were neutralized and extracted with ether. The extracts were then concentrated and the concentrates were subjected to vapor phase chromatography. In all cases a large fraction of the original ketone had condensed to high boiling material. Except for high boiling material "tails", the only peaks on the chromatograph corresponded to the starting ketones. It seemed possible that part of the ketone actually rearranged, but that all of the rearranged material rapidly condensed to high molecular weight products. However, that this was not the case was shown in two instances when the expected rearrangement product was subjected to the rearrangement conditions. In both cases starting material was recovered, although in each case there had been considerable condensation. The details of the synthesis and purification of the ketones studied are available as an internal distribution report. The compounds studied are listed below.

1. 2-methylcyclohexanone (analogous to methyl isopropyl ketone)
2. methyl cyclopentyl ketone (expected rearrangement product from 1)
3. 2,6-dimethylcyclohexanone (analogous to diisopropyl ketone)
4. methyl 2-methylcyclopentyl ketone (expected rearrangement product from 3)
5. 2,2-dimethylcyclohexanone (analogous to methyl tert-butyl ketone)

No explanation for the difference in behavior between these cyclic compounds and the analogous acyclic compounds is at hand. Additional experiments with these and related compounds are under consideration in an effort to clear up this point.

(M. Eberhardt and A. Fry)

(e) Oxygen-18 Exchange Studies With Benzopinacolone. -- As mentioned in the previous annual report, if exchange with solvent is not so fast as to make other studies meaningless, it should be possible to distinguish among several of the mechanisms of ketone rearrangements by oxygen-18 studies. Unfortunately, it has now been determined that benzopinacolone-O^{18} undergoes oxygen exchange with solvent at a very rapid rate compared to the rate of oxygen function rearrangement. Presumably the mechanism of this exchange involves reversible hydrate formation. Further work on this problem has been deferred pending results of a similar study on simpler compounds (see below).

(B. C. Menon and A. Fry)

(f) Oxygen-18 Exchange During the Rearrangement of Benzopinacol to Benzopinacolone. -- Reversible formation of benzopinacol from benzopinacol carbonium ion is probably the primary mechanism for oxygen function rearrangement of benzopinacolone (see Contract AT-(40-1)-277 Annual Progress Report, January 1, 1960, p. 30). If so, it should be possible to demonstrate this reversibility by carrying out the rearrangement and observing a decrease in the oxygen-18 content of apparently unreacted benzopinacol-O^{18} recovered after partial reaction in experiments similar to those carried out with pinacol (13). Such a study has been started using previously prepared benzopinacol-O^{18} (see Contract AT-(40-1)-277 Annual Progress Report, January 1, 1959). Preliminary experiments to select reaction conditions have been completed and the studies on the labelled compound should begin in the near future.

(A. Fry and J. Sayler)

---

(13) C. A. Bunton, T. Hadwick, D. R. Llewellyn and Y. Pocker, J. Chem Soc., 403 (1958).

2. Oxygen-18 Tracer Studies of the Mechanisms of the Displacement Reactions of Benzyl and Substituted Benzyl Alcohols.

Except for the work with p-nitrobenzyl alcohol, the original objectives of the work on the oxygen exchange between benzyl and substituted benzyl alcohols and water have now been met. This work constitutes the Ph.D. research of Dr. David Jeffrey, and an abstract of his thesis appears as Appendix XIII. The rates of exchange of anisyl alcohol-O^{18}, p-methylbenzyl alcohol-O^{18}, benzyl alcohol-O^{18} and p-chlorobenzyl alcohol-O^{18} with water have been measured at two or more different temperatures each and at sulfuric acid concentrations ranging from 0.108 M to 6.04 M. Preliminary data on p-nitrobenzyl alcohol-O^{18} indicate that it exchanges with water at a much lower rate than any of the other compounds. The experimental data are summarized in Table I. From a consideration of these data it is clear that the relative rates of the acid-catalyzed oxygen exchange of para substituted benzyl alcohols is in the order $CH_3O > CH_3 > H > Cl > NO_2$. In view of the fact that electron-donating groups in the para position have an accelerating effect on the rate, one may conclude that the benzyl carbon is more positive in the transition state than in the reactant alcohol. Further, the rate of exchange is proportional to h_o (over the range of acidities studied) for each compound, which shows clearly that the conjugate acid of the alcohol is the reacting species.

For each of the alcohols, a plot of log k_{ex} versus $-H_o$ (Hammett acidity function) gives a straight line of approximately unit slope (slightly higher than one in all cases). For each alcohol a plot of log k_{ex} versus log C_{H^+} deviates considerably from linearity. Thus, to the extent that the Zucker-Hammett hypothesis is valid, all of these compounds react by an A-1 (S_N1) mechanism; that is, the incoming water molecule is not involved in the rate-determining step.

Table I

The Rate of Oxygen-18 Exchange of Benzyl Alcohols as a Function of Acidity and Temperature

Alcohol	M H_2SO_4	Temp.(^oC)	$k_{ex} \times 10^6(sec^{-1})$
p-$CH_3OC_6H_4CH_2O^{18}H$	0.251	8.3	4.79
(0.05 M)	.504		11.97
	.999		38.5
	1.961		186.3
	0.507	20	64.9
	.108	30	40.1
	.220		90.3
	.507		226
	.736		358
	1.008		537
	1.47		1110
p-$CH_3C_6H_4CH_2O^{18}H$	0.507	90	8.07
(0.05 M)	.220	100	5.80
	.507		16.6
	1.008		45.0
	1.47		83.7
	2.01		197
$C_6H_5CH_2O^{18}H$	0.507	90	13.8
(0.10 M)	.108	100	5.77
	.504		36.2
	1.008		99.3
	1.47		201
	1.66		261
p-$ClC_6H_4CH_2O^{18}H$	0.999	80	3.49
(0.05 M)	1.961		13.05
	4.03		144.1
	5.09		498
	6.04		1568
	0.507	90	8.07
	.220	100	5.80
	.507		16.6
	1.008		45.0
	1.47		83.7
	2.01		197
p-$NO_2C_6H_4CH_2O^{18}H$	4.03	125	(12.27)
(0.05 M)			

However, the validity of the Zucker-Hammett hypothesis appears more and more questionable as data accumulates (14) and in considering our data it appeared that an alternate treatment of the A-2 (S_N2) mechanism would be more clearly diagnostic of mechanism. The relationship between acidity and rate constant for the A-2 mechanism can be expressed as follows:

$$\log k_1/a_{H_2O} = -H_o + \log \frac{f_s \, f_{BH^+}}{f_{\ddagger} \, f_B} + \text{constant}$$

The second term on the right is identical in form to the corresponding term for the A-1 mechanism, but differs in that $f_{\ddagger}$ here represents the activity coefficient of a transition state which contains a molecule of water. This logarithmic term is zero for the ideal A-1 case, and it would not be expected that the presence of water in the transition state (which, as in the A-1 case, is a univalent positive ion) would cause significantly different activity coefficient behavior in this A-2 case. Accordingly, this term should also be zero for the ideal A-2 case, and a plot of $\log k_1/a_{H_2O}$ versus $-H_o$ should be linear with a slope of unity, as contrasted to the A-1 case where a plot of $\log k_1$ versus H_o should be linear with a slope of unity.

The original objective of this work did not involve obtaining data at high enough acidities so that log k and $\log k/a_{H_2O}$ would be significantly different, so the work has been extended to higher acidities

---

(14) See, for instance, R. W. Taft, "Preprint, Division of Petroleum Chemistry," 5, 133, 137th Meeting Am. Chem. Soc. (1960), and N. C. Deno, T. Edwards and C. P. Perizzolo, J. Am. Chem. Soc., 79, 2109 (1957).

for those compounds (containing electron withdrawing groups) which would be most likely to react by the A-2 mechanism. For p-chlorobenzyl alcohol-O^{18} at 80° (see Table I) a plot of log k_{ex} versus $-H_o$ is linear up to 6 M sulfuric acid, while a plot of log k_{ex}/a_{H_2O} versus $-H_o$ deviates significantly from linearity. Thus, the indication by either criterion is that p-chlorobenzyl alcohol is reacting by the A-1 mechanism. Data for p-nitrobenzyl alcohol-O^{18} at high acidities is now being accumulated. This is the compound which would be the most likely of any of the series to react by the A-2 mechanism.

A survey is being made of data in the literature to see if this proposal (that linearity of a plot of log k/a_{H_2O} versus $-H_o$ is characteristic of an A-2 reaction) has merit. In many reactions thought to go by the A-1 mechanism, a plot of log k versus $-H_o$ is linear while a plot of either log k versus log C_{H^+} or log k/a_{H_2O} versus $-H_o$ is not linear. But for the more critical A-2 cases, most of the data are not accurate enough or are not carried to high enough acidities to be useful. However, the data of Bell, Dowding and Noble (15) on the hydrolysis of ethyl acetate and of Chmiel and Long (16) on the hydrolysis of α-glyceryl mono-3,4,5-trimethoxybenzoate give better straight lines when plotted as log k/a_{H_2O} versus $-H_o$ than as log k versus log C_{H^+} or as log k versus $-H_o$. This is encouraging, but more data will need to be accumulated before a definite conclusion can be drawn. A bothersome feature of the log k/a_{H_2O} versus $-H_o$ plots is

---

(15) R. P. Bell, A. L. Dowding and J. A. Noble, J. Chem. Soc., 3106 (1955).

(16) C. T. Chmiel and F. A. Long, J. Am. Chem. Soc., 78, 3326 (1956).

that the slopes deviate considerably from unity. It is probably this feature which led Zucker and Hammett (17) to reject this type of plot in their original work.

(D. Jeffrey, R. Haynes and A. Fry)

3. Oxygen-18 Tracer Studies of the Exchange Between Water and the Carbonyl Oxygen of Ketones.

The hope that oxygen-18 tracer studies would be helpful in determining the mechanisms of ketone rearrangements (see above) coupled with our interest in the effects of substituents on the rates of reactions (eg., the benzyl alcohol studies above and the benzyl chloride studies below) led us to initiate a program of studying the oxygen exchange between substituted benzophenones and water:

$$XC_6H_4CO^{18}C_6H_5 + H_2O \rightleftharpoons XC_6H_4COC_6H_5 + H_2O^{18}$$

The substituents, X, chosen are the same as those used in the benzyl alcohol and benzyl chloride studies, namely, CH_3O, CH_3, H, Cl and NO_2, with the possible additions of others.

Benzophenone-O^{18}, p-methoxybenzophenone-O^{18}, p-methylbenzophenone-O^{18}, p-chlorobenzophenone-O^{18} and p-bromobenzophenone-O^{18} have been prepared either by base-catalyzed exchange with water-O^{18} or by hydrolysis of the appropriate dichloromethane with water-O^{18}. Preliminary experiments at 50° with benzophenone-O^{18} dissolved in 90% dioxane-10% water solutions showed that exchange was very slow in the absence of acid or base, quite rapid when the solution was 0.1 M in either sodium hydroxide or perchloric acid, and conveniently measurable when the solution was 0.01 M in perchloric acid. The p-CH_3O,

---

(17) L. Zucker and L. P. Hammett, J. Am. Chem. Soc., 61, 279 (1939).

p-CH_3, p-Cl and p-Br compounds were also shown to exchange at a measurable rate under the latter conditions. Kinetic studies have been made on benzophenone-O^{18} and p-chlorobenzophenone-O^{18} under these conditions, and good first order plots were obtained. The rate constants are 6.79×10^{-5} $sec.^{-1}$ and 3.32×10^{-5} $sec.^{-1}$, respectively. Preparation of the p-NO_2 compound is in progress, and the exchange experiments on it and the other compounds are planned for the near future. The variation of the rates with acid concentration and the rates of the base catalyzed exchange may also be investigated.

(B. C. Menon and A. Fry)

D. ISOTOPE EFFECT STUDIES

1. Isotope Effects in the Displacement Reactions of Benzyl and Substituted Benzyl Halides.

Work on the chlorine isotope effects in the displacement reactions of benzyl and substituted benzyl chlorides with various nucleophiles has now been completed, and a paper reporting the results is in preparation. This work constitutes the Ph.D. research of Dr. John Hill, and an abstract of his thesis appears as Appendix XIV. The results of this study show for the first time a definite relationship between isotope effect and kinetic order of a reaction, and hence, such isotope effects can now be used as a criterion of mechanism. The pertinent kinetic and isotope effect results are shown in Tables II and III, respectively.

Examination of these data show that a good qualitative correlation exists between the kinetic order of a given reaction and the magnitude of the kinetic isotope effect observed for that reaction. Those reactions exhibiting first order kinetics gave isotope effects (k^{35}/k^{37}) of approximately 1.0073, while those which were kinetically second order exhibited isotope effects close to 1.0054. Those reactions which displayed mixed order kinetics gave isotope effects intermediate in magnitude between the above values.

Table II

Rate Constants for the Reactions of Benzyl and Substituted Benzyl Chlorides with Various Nucleophiles in 80 Percent Aqueous Dioxane at 30°

[KCN] = 0.05002 m $[Na_2S_2O_3]$ = 0.05001 m $[p\text{-}XC_6H_4CH_2Cl]$ = 0.1000 m

	Added Nucleophile		
Substituent	None[a]	CN^-	$S_2O_3^=$
CH_3O	262	424[a]	534[a]
CH_3	0.252	0.413[a]	---
H	0.0466	---	---
Cl	0.0374	---	0.348[b]
NO_2	0.0129	0.839[b]	1.18[b]

[a] $k_1(hr.^{-1} x10^3)$

[b] $k_2(l.mole^{-1}\ hr.^{-1})$

Table III

Chlorine Isotope Effects (k^{35}/k^{37}) in the Reactions of Benzyl and p-Substituted Benzyl Chlorides with Various Nucleophiles in 80 Percent Aqueous Dioxane

		Added Nucleophile		
Substituent	Temperature	None	CN^-	$S_2O_3^=$
CH_3O	30	1.0072	1.0074	1.0075
CH_3	30	1.0071	1.0073	1.0069
H	30	1.0074	1.0068	1.0060
	50	1.0073	---	---
Cl	30	1.0074	1.0056	1.0055
NO_2	30	1.0072	1.0054	1.0054
	50	---	1.0054	---
	90	1.0073	---	---

precision ± ~0.0002

The hydrolysis of benzyl chloride at 50°, that of p-nitrobenzyl chloride at 90°, and the reaction of the latter with potassium cyanide at 50° were also studied. The isotope effects observed for these reactions were the same as those observed for the corresponding reactions at 30°. Hence, there is little or no temperature dependence for the kinetic isotope effects over this range.

Attempts to correlate the observed isotope effects with theory were not very fruitful. The Bigeleisen equation (18) predicts much larger isotope effects and larger temperature coefficients than those observed when the usual, admittedly oversimplified models are employed. Considerable experimentation was done with various models for the theoretical calculations. In no case was reasonable agreement with experiment obtained. It appears to us that for such complicated systems, there is little hope of ever being able to construct reasonable models for the S_N1 and S_N2 mechanisms which will predict unambiguously differences such as those observed. The empirical correlation, however, is very striking and should prove to be very useful.

(J. Hill and A. Fry)

The extension of this effort to distinguish between reaction by the S_N1 or the S_N2 mechanism by chlorine isotope effect measurements to strictly aliphatic compounds is planned for the near future. n-Butyl chloride presumably reacts by an S_N2 mechanism, t-butyl chloride by an S_N1 mechanism and sec-butyl chloride by a "borderline" mechanism. If the empirical correlation idea noted above is correct,

---

(18) J. Bigeleisen, J. Chem. Phys., 17, 675 (1949); J. Bigeleisen and M. Wolfsberg, ibid., 21, 1972 (1953), 22, 1264 (1954).

the chlorine isotope effects for the three compounds should be in the order t-butyl > sec-butyl > n-butyl. Work with other series of compounds is also being considered.

(A. Fry)

2. Isotope Effects in the S_N2' Reaction.

3-Chloro-1-butene-1-C^{14} has been prepared by the procedure outlined in the previous annual report, and the carbon-14 isotope effect in its S_N2' reaction with diethyl amine has been measured. The value for k^{12}/k^{14} is 1.057 ± 0.007. Similar measurements are planned for the 3-chloro-1-butene labelled at the other positions at which bonding changes occur (carbons 2 and 3, nitrogen and chlorine). The work on the chlorine isotope effect will be done in the immediate future.

(M. Eberhardt, M. Bufalini and
A Fry)

3. Isotope Effect Study of the Curtius Rearrangement.

Work on this problem during the past year has been concentrated on the nitrogen isotope effect in the evolved nitrogen gas. Considerable difficulty was encountered in obtaining consistent results because of mass-spectrometer trouble, but recent preliminary results show conclusively that there is an isotope effect. The value for k^{14}/k^{15} is about 1.02. The procedure for obtaining nitrogen gas from the benzamide for measurement of the nitrogen isotope effect at the amide nitrogen has also been worked out, but no isotope effect measurements have been made.

(J. Wright and A. Fry)

PART II. INSTRUMENTATION AND FACILITIES

During the past year the accelerator has operated dependably with no unscheduled down time except for the time required to replace an ion gage that failed. Approximately 48 hours were devoted to proton bombardments in connection with a research project in the Physics Department of this university. About 102 running hours of deuteron bombardments were used, 18 freshly mounted Zr-H^3 targets being consumed in the process.

As reported in the previous annual report the arc-type ion source normally used produces only about 10-20% of monatomic deuterium ions, the rest consisting of approximately equal amounts of the di- and the triatomic species. In an attempt to increase the neutron flux an RF-type ion source is currently under investigation. It is essentially the type described by Moak (19). This source should deliver from 1 to 2 milliamperes of beam current, of which over 90% should be the monatomic species. For several weeks we were not able to draw more than 30-40 microamperes from this source. Then it was noticed that there must have been an error in the original article pertaining to the solenoid surrounding the extracting end of the ion source. By increasing the number of turns of No. 22 wire from 25 (as stated in the article) to about 600, the beam current could be increased to over 200 microamperes. Our experience indicates that the beam current is very sensitive to the design of the solenoid and of the extractor probe. These are being redesigned now and will be tested further in the near future.

To facilitate the study of short-lived isotopes a pneumatic sample transport system has been designed and installed. With this

---

(19) C. D. Moak, H. Reese, Jr. and W. M. Good, Nucleonics 9, No. 3, 18 (1951).

system a sample can be sent to an irradiation station in front of the target plate on the accelerator, irradiated, and then sent to a counting station all by remote control. The transit time for the sample carrier to travel about 130 feet from the accelerator to the counter is less than 2.5 seconds. With this system the 0.8 second Pb^{207} activity was easily followed for several half-lives.

A photocell system is now being installed so that the operator will definitely know that the sample carrier is in the proper irradiation position, and also so that the time that the bombardment ends can be determined accurately. A vacuum cleaner is used to supply the pressure differential, and has been found to operate quite successfully.

One 2" x 2" NaI(Tl) well crystal and one 3" x 3" NaI(Tl) crystal were purchased this year. The latter was an Integral Line Assembly purchased from Harshaw Chemical Co. The old 3" x 3" NaI(Tl) crystal was found to have lost part of its optical coupling with its window, and it was sent to Harshaw to be remounted in another Integral Line Assembly.

The Eldorado 50-channel pulse-height analyzer, described in the previous annual report as never having operated properly for any useable length of time during the last contract year, was converted to a 30-channel analyzer. It was hoped that this would relieve the overloaded components, allowing the instrument to be used. Unfortunately the device still remained useless despite constant attention from the University of Arkansas' electronics shop. The decision was made to purchase a new multichannel analyzer, and the type chosen was the Radiation Instrument Development Laboratory's 200-channel transistorized model. The instrument has just been delivered in good operating condition and we are now in a position to broaden the scope of our research program to include nuclear decay scheme studies.

An instrument for testing the rectifiers in the power supply of the Cockcroft-Walton accelerator while under full load current has been designed and constructed by the University of Arkansas' electronics shop.

A new air-conditioned counting room and office next to the accelerator laboratory has been added to the facilities of the nuclear chemistry group. This room will also be connected to the pneumatic transport system described above.

A constant temperature bath was purchased to be used in the radiation damage to plastics studies. Viscosity measurements are used to evaluate the damage, and an accurately controlled temperature bath is a necessity.

PART III. PERSONNEL

NUCLEAR CHEMISTRY AND PHYSICS

Staff

Fink, Prof. R. W. (On off campus duty assignment and leave of absence, Gustaf Werner Institute for Nuclear Chemistry, University of Uppsala, Sweden until December 1960)

Gardner, Prof. D. G.

Kuroda, Prof. P. K.

Kantele, Dr. J., Postdoctoral appointment (effective September 1960; see biographical information below)

Graduate Students

Bramlitt, Edward T., B.S. 1956 University of the South; M.S. University of Tennessee. Problem: Study of neutron reactions in the region of neutron shell N = 50. (Ph.D. candidate)

Chittenden, David M., B.S. 1958 Rensselaer Polytechnic Institute; M.S. 1960 University of Arkansas. Problem: Energy and angular distribution of particles from fast neutron reactions. (Ph.D. candidate)

Broom, Knox M., B.S. 1958 Mississippi Southern. Problem: 14 Mev neutron induced fission. (M.S. candidate)

Poularikas, A., B.S. 1960 University of Arkansas. Problem: (n,t) reactions induced by 14.8 Mev neutrons. (M.S. candidate)

Smith, C. Fred, B.S. 1959 Abilene Christian College, Problem: Energy transport in copolymers of polymethylmethacrylate and α-methyl styrene. (M.S. candidate)

Das, Ghanta Krishna, B.Sc. 1955 Sir C. R. Reddy College, Eluru, India.

Research Assistants

Wray, J. E., Accelerator Specialist

Culp, G.

Jinks, C.

Nix, J. (Undergraduate research participation program, summer 1960)

THEORETICAL PHYSICS

Staff

Schwartz, Prof. H. M.
Scroggs, Prof. J. E.

Graduate Students

McMillan, William L., B.S. (Elec. Eng.) 1957 University of Arkansas. Problem: Molecular dissociation in β-decay. (M.A. expected January, 1961)

Research Assistants

Gardner, Mrs. J. C., M.S. (Math) 1959 University of Pittsburgh (effective June, 1960)
Davidson, Miss Cheri L. (terminated June, 1960).

ORGANIC CHEMISTRY

Staff

Fry, Prof. Arthur
Eberhardt, Dr. M. (terminated Nov. 30, 1960)

Graduate Students

Jeffrey, David A., B.S. 1952 Acadia University; M.S. 1957 University of Arkansas. Problem: The kinetics of oxygen exchange of substituted benzyl alcohols as a function of acidity. (Ph.D. expected January 1961) (Now Assistant Professor of Chemistry, Arlington State College, Arlington, Texas)

Hill, John M., B.S. 1957 Middle Tennessee State College; National Science Foundation Fellow, 1960-61. Problem: Chlorine isotope effects in the reactions of benzyl and substituted benzyl chlorides with various nucleophiles. (Ph.D. expected January 1961) (Now Assistant Professor of Chemistry, Northeast Louisiana State College, Monroe, Louisiana)

Wright, Joe C., B.S. 1954 Ouachita College. Problem: Isotope effect study of the Curtius Rearrangement. (M.S. candidate)

Ookuni, Ikuo, B.S. 1953, M.S. 1956 Rikkyo (St. Paul's) University, Tokyo, Japan. Problem: Mechanism of acid-catalyzed rearrangements of aliphatic ketones.

Menon, B. C., B.Sc. 1958 University of Rangoon, Burma. Problem: Oxygen-18 tracer studies of ketone rearrangements. (M.S. candidate)

Barnes, Robert B., B.A. 1957 Central College. Problem: The mechanism of the acid catalyzed rearrangements of 3,3-dimethyl-2-butanone-1-C^{14} and 3,3-dimethyl-2-butanone-2-C^{14}. (Ph.D. candidate)

Research Assistants

Bufalini, Mrs. Marijon M., B.S. 1957, M.S. 1959 University of Arkansas

Haynes, R. (NSF undergraduate research participation program, summer, 1960)

Sayler, Mrs. J. R. (NSF undergraduate research participation program, summer, 1960)

BIOGRAPHICAL DATA ON NEW STAFF MEMBERS

Kantele, P. Juhani, Research Collaborator (postdoctoral)

Education:

M.Sc. 1956 University of Helsinki, Finland
Ph.D. 1959 University of Helsinki, Finland

Experience:

Assistant (teaching and research), Institute of Physics, University of Helsinki, Finland, 1956-1960.

Publications:

J. Kantele, "On the Level Structure of B^{10}," Ann. Acad. Scient. Fenn. A VI, 37 (1959).

R. W. Fink, G. Andersson and J. Kantele, "Nuclear Spectroscopy of Mass Separated Neutron-Deficient Tellurium Isotopes," Ark. Fys., in publication.

PART IV. PUBLICATIONS AND PARTICIPATION IN PROFESSIONAL MEETINGS

A. PUBLISHED, IN PRESS AND SUBMITTED FOR PUBLICATION

1. D. M. Chittenden, D. G. Gardner and R. W. Fink, A New Isotope of Manganese; Cross-sections of the Iron Isotopes for 14.8 Mev Neutrons, Phys. Rev., submitted, 1960.

2. C. T. Davis and A. Fry, Oxygen Function Rearrangement in 3,3-Dimethylbutan-2-one-[2-^{14}C], Chem. & Ind. (London), 227 (1960).

3. R. W. Fink, G. Andersson and J. Kantele, Nuclear Spectroscopy of Mass Separated Neutron-Deficient Tellurium Isotopes, Arkiv for Fysik, submitted, 1960.

4. A. Fry, M. Eberhardt and I. Ookuni, Acid-Catalyzed Rearrangement of Diethyl Ketone and Diisopropyl Ketone, J. Org. Chem., 25, 1252 (1960).

5. D. G. Gardner and L. M. Epstein, Protection Against Radiation Damage in Polymethylmethacrylate By High Energy Electrons and By Ultraviolet Light, J. Chem. Phys., in press, 1960.

6. I. Kumabe and R. W. Fink, The Angular and Energy Distribution of Protons from Ni^{58} Reactions Induced by 14.8 Mev Neutrons, Nuclear Phys. 15, 316 (1960).

7. I. Kumabe, A. D. Poularikas, I. L. Preiss, D. G. Gardner and R. W. Fink, (n,He^3) Reactions of Medium Weight Nuclei Induced by 14.8-Mev Neutrons, Phys. Rev. 117, 1568 (1960).

8. A. Poularikas, J. Cunningham, W. McMillan, J. McMillan and R. W. Fink, New Isomers of Scandium-50 and Indium-120; Gamma-rays in Lutecium-178 Decay, J. Inorg. and Nuclear Chem. 13, 196 (1960).

9. A. Poularikas, S. Umemoto, E. Bramlitt and D. G. Gardner, Some Additional (n,He^3) Reactions Induced By 14.8 Mev Neutrons, Phys. Rev., submitted, 1961.

10. I. L. Preiss and R. W. Fink, New Isotopes of Cobalt; Activation Cross-sections of Nickel, Cobalt and Zinc for 14.8 Mev Neutrons, Nuclear Phys. 15, 326 (1960).

11. H. M. Schwartz, Ritz-Hylleraas Solutions of the Ground State of Two-Electron Atoms Involving Fractional Powers, Phys. Rev. 120, 483 (1960).

12. R. G. Wille and R. W. Fink, Activation Cross-Sections for 14.8-Mev Neutrons and Some New Radioactive Nuclides in the Rare Earth Region, Phys. Rev., 118, 242 (1960).

B. Ph.D. THESES

1. John William Hill, Chlorine Isotope Effects in the Reactions of Benzyl and Substituted Benzyl Chlorides with Various Nucleophiles. (Director, A. Fry)

2. David Austin Jeffrey, The Kinetics of Oxygen Exchange of Substituted Benzyl Alcohols as a Function of Acidity. (Director, A. Fry)

C. MASTERS THESES

1. David M. Chittenden II, Neutron Activation Cross-sections of Iron Isotopes at 14.8 Mev. (Director, D. G. Gardner)

2. Charles T. Davis, The Mechanism of the Acid Catalyzed Rearrangement of 3,3-Dimethyl-2-butanone-2-C^{14}. (Director, A. Fry)

3. William L. McMillan, Probabilities of Rotational-Vibrational Dissociation of a Diatomic Molecule in Beta Decay. (Director, H. M. Schwartz)

D. PAPERS PRESENTED AT MEETINGS

1. R. W. Fink, Recent Developments in Orbital Electron Capture, invited seminar, Department of Physics, University of Uppsala, Sweden, March, 1960.

2. R. W. Fink, Fast Neutron Research with the Arkansas Accelerator, invited seminar, Institut fur Radiumforschung und Kernphysik, Vienna, Austria, November, 1960.

3. R. W. Fink, Fast Neutron Research with the Arkansas Accelerator, invited seminar, Experimentalphysik Institut of the Physikalisches Staatsinstitut, Hamburg, Germany, December 2, 1960.

4. R. W. Fink, Nuclear Spectroscopy of Tellurium with Mass Separated Sources, invited seminar, Department of Physics, Yale University, New Haven, Conn., December 14, 1960.

5. A. Fry, Mechanisms of Ketone Rearrangements, invited seminar, Department of Chemistry, Oklahoma State University, Stillwater, Okla., December 15, 1960.

6. A. Fry and C. T. Davis, Oxygen Function Rearrangement in 3,3-Dimethyl-2-butanone-2-C^{14}, 44th Annual Meeting, Arkansas Academy of Science, Russellville, Ark., April 1-2, 1960.

7. A. Fry, M. Eberhardt and I. Ookuni, Acid-Catalyzed Rearrangement of Diethyl Ketone and Diisopropyl Ketone, 137th National Meeting, American Chemical Society, Cleveland, Ohio, April 5-14, 1960.

8. A. Fry and J. Hill, Chlorine Isotope Effects in Displacement Reactions of Benzyl Chlorides, Gordon Research Conference on Chemistry and Physics of Isotopes, New Hampton, N.H., July 4-8, 1960.

9. D. G. Gardner and L. M. Epstein, Protection Against Radiation Damage in Polymethylmethacrylate Caused By High Energy Electrons and By Ultraviolet Light, American Physical Society, Detroit, Mich., March 21-25, 1960.

10. J. Hill and A. Fry, Chlorine Isotope Effects in the Reactions Between Benzyl Chlorides and Various Nucleophiles, 16th Southwest Regional Meeting, American Chemical Society, Oklahoma City, Okla., December 1-3, 1960.

11. D. Jeffrey and A. Fry, Oxygen-18 Exchange Studies of Benzyl Alcohols as a Function of Acidity, 138th National Meeting, American Chemical Society, New York, N.Y., September 11-16, 1960.

12. A. Poularikas, I. Kumabe, I. L. Preiss, D. G. Gardner and R. W. Fink, (n,He^3) Reactions in Medium Weight Nuclei Induced By 14.8 Mev Neutrons, American Physical Society, Houston, Texas, March 4-5, 1960.

13. H. M. Schwartz, On a Quasi-Empirical Method of Estimating the Accuracy of the Ground State Energy of the Helium Atom, 1960 Annual Meeting of the American Physical Society, January 27-30, 1960.

APPENDIX I.

D. M. Chittenden II, D. G. Gardner and R. W. Fink

A New Isotope of Manganese; Cross-Sections of the Iron Isotopes for 14.8 Mev Neutrons

Submitted for Publication, 1960

Preprint

A New Isotope of Manganese; Cross-Sections of the Iron Isotopes for 14.8 Mev Neutrons*

D. M. Chittenden II, D. G. Gardner and R. W. Fink**
Department of Chemistry, University of Arkansas, Fayetteville, Ark.

ABSTRACT

Bombardment of iron enriched in Fe^{58} with 14.8 Mev neutrons produces an activity having a half-life of 1.1 ± 0.1 min. On the basis of cross-bombardments and the gamma ray spectrum of the activity, this is assigned to Mn^{58}. In addition, the following cross-sections were measured: Fe^{58} (n,p), 23.0 ± 3.5 mb; Fe^{57} (n,p), 71.0 ± 7.0 mb; Fe^{56} (n,p), 128 ± 13 mb; Fe^{58} (n,α), 21.5 ± 2.0 mb; Fe^{54} (n,α), 270 ± 135 mb; Fe^{57} (n,np), 6.1 ± 2.6 mb; Fe^{54} (n,2n), 7.9 ± 0.8 mb; Fe^{54} (n,t), 0.6 ± 0.1 mb. The experimental cross-sections were found to differ significantly from those which were calculated from the statistical evaporation model of the compound nucleus.

INTRODUCTION

The work of Preiss and Fink (1), of this laboratory, indicates

---

(1) I. L. Preiss and R. W. Fink, Nuclear Phys. 15, 326 (1960).

---

*Supported in part by the U.S. Atomic Energy Commission. This work constitutes part of the M.S. thesis of D. M. Chittenden II at the University of Arkansas.

**Visiting scientist at Gustaf Werner Institute for Nuclear Chemistry, University of Uppsala, Sweden, 1959-1960.

that there is a marked effect of shell structure on the probabilities for the occurrence of 14.8 Mev neutron induced reactions in the region Z = 28. Levkovskii (2) has reported a trend of absolute (n,p) and (n,α) cross-sections with mass number. The cross-section of various isotopes of an element usually decrease by a factor of 2, 4, or 8 with increasing mass number. This variation is more pronounced in the light elements. The present work was undertaken as part of a program to study 14.8 Mev neutron-induced reactions around the closed 28 neutron shell, and also to examine another region where trends such as noted by Levkovskii might be encountered.

EXPERIMENTAL

Cross sections were measured with 14.8 ± 0.9 Mev neutrons (10^{10} - 10^{11} neutrons/sec) from the T(d,n)He^4 reaction at 0° to the incident deuteron beam of the University of Arkansas 400KV Cockcroft-Walton accelerator. Bombardment periods ranged from 30 sec - 6 hrs.

Enriched Fe^{54}, Fe^{57}, and Fe^{58}, in the form of the powder Fe_2O_3 and natural iron foil (91.6% Fe^{56}) were irradiated. Copper and aluminum foils where used as monitors utilizing the accurately determined cross-sections of Cu^{63} (n,2n) Cu^{62} reaction (556 mb) determined by Yasumi (3) and the Al^{27} (n,α) Na^{24} reaction (114 mb) determined by Poularikas and Fink (4). Sample thicknesses were 10-55 mg/cm².

---

(2) V. N. Levkovskii, Sov. Phys. JETP 6, 1174 (1958); 4, 291 (1957).

(3) S. Yasumi, J. Phys. Soc. Japan 12, 433 (1957).

(4) A. Poularikas and R. W. Fink, Phys. Rev. 115, 989 (1959).

Table I.

Absolute Neutron Activation Cross Sections at 14.8 Mev for the Isotopes of Iron

Reaction			Measured Cross Section (mb)				
Reaction	Product	Measured Half-Life	Present Work	Other Work	Q-Value (Mev)	Calculated Cross Section (mb)	Ratio $\sigma_{exp}/\sigma_{calc}$
$Fe^{54}(n,t)$	Mn^{52m}	21 ± 2 min	0.6 ± 0.1		- 11.5	--	--
$Fe^{54}(n, 2n)$	Fe^{53}	8.4 ± 0.4 min	7.9 ± 0.8	10(a) and 2(b)	- 13.6	483	0.016
$Fe^{54}(n,\alpha)$	Cr^{51}	25 ± 5d	270 ± 135		+ 0.8	13.0	20.8
$Fe^{54}(n,p)$	Mn^{54}	300d (a)		400 (a)	+ 0.2	31.2	14.7
$Fe^{56}(n,p)$	Mn^{56}	2.56 ± 0.11 hrs	128 ± 13	96.7(c) 124 ± 12 (d)	- 2.9	8.2	15.6
$Fe^{57}(n,p)$	Mn^{57}	1.5 ± 0.1 min	71.0 ± 7.0		- 1.9	60.7	1.17
$Fe^{57}(n,np)$	Mn^{56}	2.56 ± 0.20 hrs	6.1 ± 2.6		- 10.5	4.86×10^{-4}	1.25×10^{4}
$Fe^{58}(n,p)$	Mn^{58}	1.1 ± 0.1 min	23.0 ± 3.5		- 5.2	1.80	12.8
$Fe^{58}(n,\alpha)$	Cr^{55}	3.5 ± 0.1	21.5 ± 2.0		- 1.5	2.4	8.95

(a) D. L. Allen, Proc. Phys. Soc. (London) A70, 196 (1957).

(b) B. L. Cohen, Phys. Rev. 81, 184 (1951).

(c) E. B. Paul and R. L. Clark, Can. J. Phys. 31, 267 (1953).

(d) S. G. Forbes, Phys. Rev. 88, 1309 (1952).

(*) Calculated from data of K. Way, R. W. King, C. L. McGinnis, R. Van Lieshout, AEC Document TID-5300, June, 1955.

Bombardment of $Fe_2^{57}O_3$ (76.7% Fe^{57}) gave rise to the 1.5 ± 0.1 min. activity from the $Fe^{57}(n,p)Mn^{57}$ reaction and 2.55 ± 0.05 hur. activity from the $Fe^{56}(n,p)Mn^{56}$ and $Fe^{57}(n,np)Mn^{56}$ reaction.

The activities observed upon irradiation of enriched $Fe_2^{54}O_3$ (96.66%) were 8.4 ± 0.4 min Fe^{53} from the (n,2n) reaction, 25 ± 5d Cr^{51} from the (n,α) reaction, and 21 ± 2 min. Mn^{52m} from the (n,t) reaction. The previously reported 2.1 min activity assigned to Mn^{54m} (7) was not observed.

DISCUSSION

In Table I the observed values of the cross sections are compared with the values computed from the theory of Blatt and Weisskopt (8).

The (n,p) reactions were found to exhibit the trend observed by Levkovskii (2). Thus, the (n,p) cross sections go as Fe^{54}: Fe^{56}: Fe^{57}: Fe^{58}:: 3.6 : 1.0 : 0.55 : 0.18. Poularikas and Fink (9) have

---

(5) C. E. McFarland, F. B. Schull, A. J. Elevyn, B. Zudman, Phys. Rev. 99, 655 (1955).

(6) A. Sperduto, W. W. Buechner, Bull. Am. Phys. Soc. 1, No. 4 2 3W4 (1956).

(7) D. O. Caldwell and H. F. Stoddart, Phys. Rev. 81, 666 A (1951).

(8) J. M. Blatt and V. F. Weisskopt, Theoretical Nuclear Physics, John Wiley and Sons, New York, 1952.

(9) A. Poularikas and R. W. Fink, Phys. Rev. 115, 989 (1959).

suggested that these trends might be explained qualitatively on the basis of direct interaction with neutrons outside of a closed shell in the target nucleus, so that the decreasing (n,p) trend reflects increasing competition from the neutron emitting reactions as A increases at constant Z. Because of the large uncertainty in the cross section for the $Fe^{54}(n,\alpha)Cr^{51}$ reaction, due primarily to uncertainty in the counting efficiency for Cr^{51} x-rays in the counter use here, it is not possible to examine the ratio of the (n,α) cross sections of Fe^{54} to Fe^{58} for a Levkovskii factor of 2^n.

The ratios of the experimental to the calculated cross sections shown in Table I, are larger than 1 for the (n,p), (n,α), and (n,np) reactions and much less than 1 for the single (n,2n) crosssection measured here.While the ratios (1) for the (n,2n) reaction on other isotopes in this mass range also tend to be less than 1 (Co^{59} : 0.41, Ni^{58} : 0.16, Zn^{64} : 0.91), none are quite as small as that for Fe^{54}. This may be due in part to the fact that Fe^{54} has a closed neutron shell of N = 28. For the other reactions, ratios in excess of 1 are usually taken to indicate that direct interaction processes are present and important. For the elements Fe, Co, and Ni, we are concerned with the filling of the $1f^{7/2}$ proton shell. For Cu and Zn the 2p 3/2 proton shell is beginning to be filled. Preiss and Fink (1) have shown that the experimental to calculated cross section ratios for the (n,p) reaction exceed 1 for Cu and Zr, but are less than 1 for Ni and Co. Considering the proton shell closure at Ni, it might be expected that the cross section ratios would exceed 1 for Fe, Co, Cu, and Zn. A study of the experimental (n,p) cross section trends for the five elements clearly shows that the Ni cross sections are indeed much lower than expected (10). It is not clear, however, why the ratio for Co. should be less than 1.

The exceedingly large cross section ratio for the $(n,\alpha p)$ reaction on Fe^{57}, and the observation of the (n,t) reaction on Fe^{54} lend further support to the nuclear cluster theory of Wilkinson (11) and others (12).

The authors wish to acknowledge the assistance of Mr. J. E. Wray of the Accelerator Laboratory for operation of the accelerator.

---

(10) To be published.

(11) D. H. Wilkinson, Phil. Mag. 4, 215 (1959).

(12) K. Wildemuth and H. Kenellopoulis, CERN-59-23 (June 5, 1959).

APPENDIX II.

R. W. Fink, G. Andersson and J. Kantele

Nuclear Spectroscopy of Mass Separated Neutron-Deficient Tellurium Isotopes

Submitted to Arkiv for Fysik, 1960

Abstract and Proposed Decay Schemes

Nuclear Spectroscopy of Mass Separated Neutron-Deficient Tellurium Isotopes

By R. W. Fink*, G. Andersson and J. Kantele*

The Gustaf Werner Institute for Nuclear Chemistry
University of Uppsala
Uppsala, Sweden

ABSTRACT

The radioactive decay of five neutron-deficient activities of tellurium from irradiations of Sb with 90 - 140 MeV protons has been investigated with magnetic and scintillation spectrometers, beta proportional counter, and alpha ionization chamber using mass separated sources.

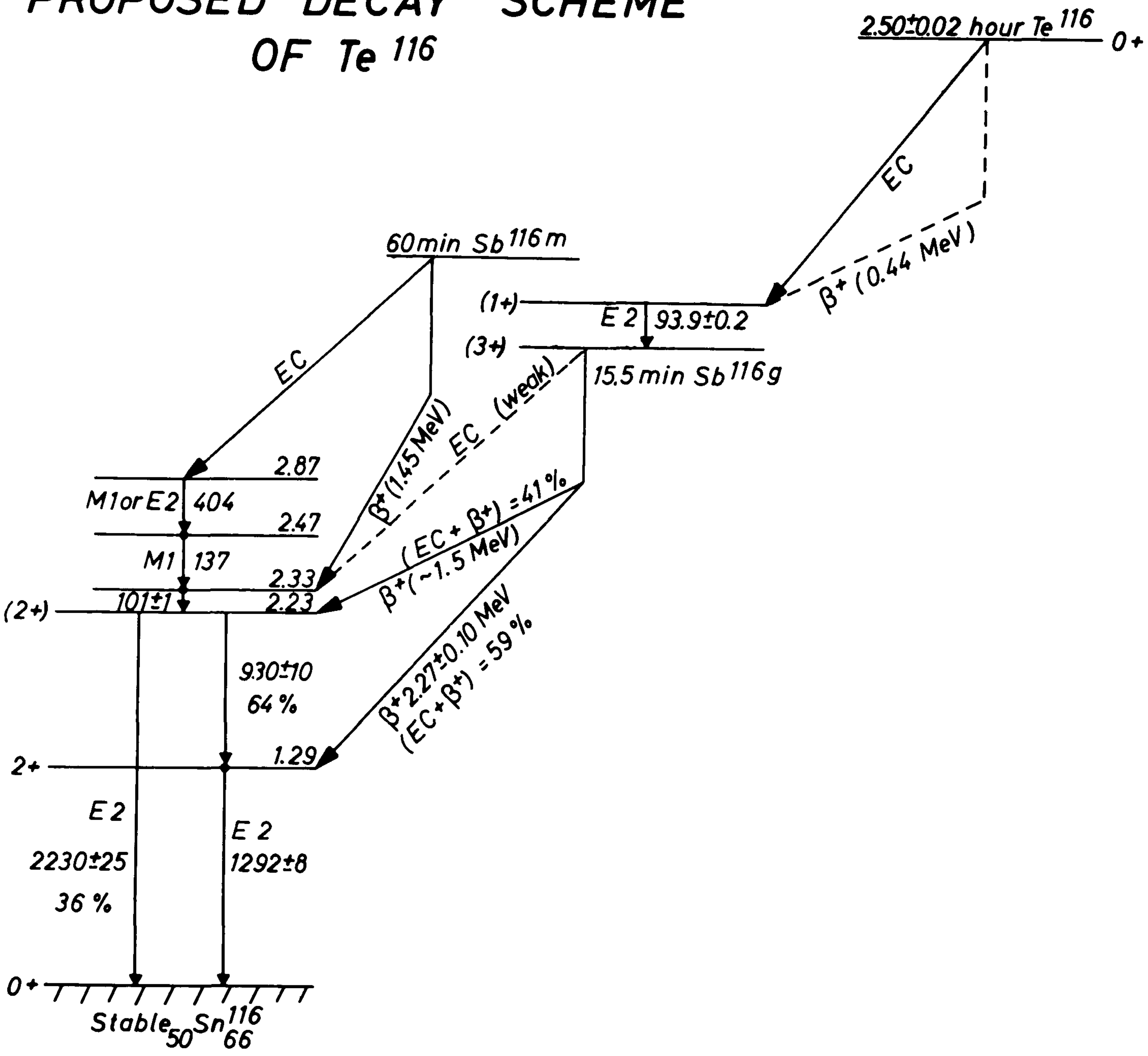
The electron spectra and the gamma scintillation singles and coincidence spectra have been interpreted in the form of tentative disintegration schemes to account for the decay modes of Te^{116} (2.50 ± 0.02 hours), Te^{117} (61 ± 2 minutes, measured spin 1/2), Te^{118} (6.00 ± 0.02 days), and Te^{119} isomers (15.9 ± 0.3 hours, measured spin 1/2; and 4.5 ± 0.3 days, measured spin 1-1/2). Two neutron-deficient Sb isotopes also were prepared by mass separation of antimony metal and their half-lives confirmed: Sb^{115} (36 ± 3 minutes) and Sb^{116} (64 ± 4 minutes). From $\mathrm{NH_4I}$ targets irradiated with 145 - 180 MeV protons, a new Te activity was found with half-life about 5 - 6 minutes, which might be Te^{115} or Te^{114}. A new carrier-free radiochemical separation technique requiring about 30 seconds is reported for preparing Te sources from the irradiated $\mathrm{NH_4I}$ targets.

No isomer in Te^{117} having a half-life greater than 15 minutes was detected, and in the case of the Te^{119} isomers, no transitions corresponding to the internal branch could be found, the two isomers apparently decaying independently to levels in antimony.

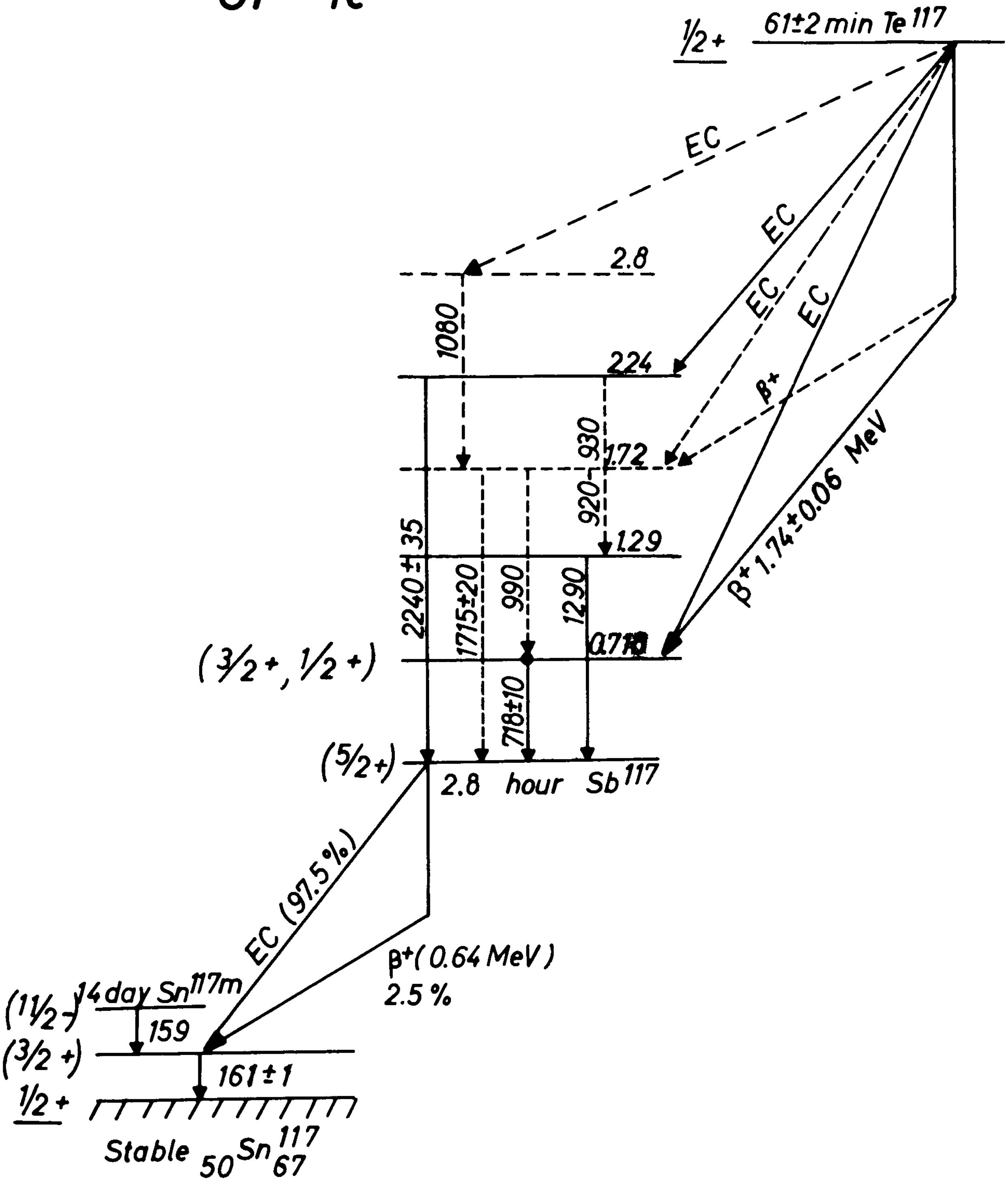
---

* Present address: Department of Chemistry, University of Arkansas, Fayetteville, Arkansas, USA.

PROPOSED DECAY SCHEME OF Te^{116}

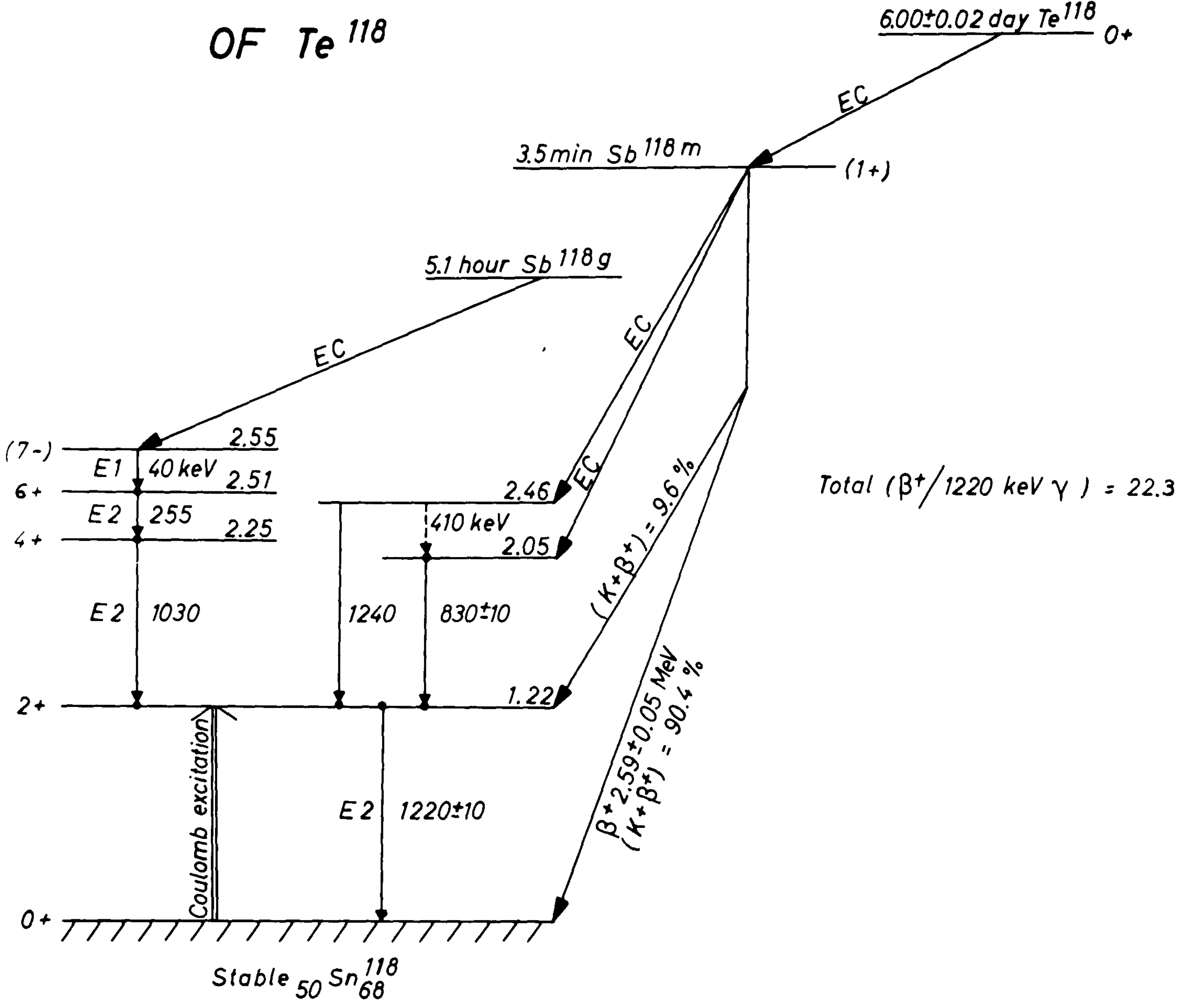


PROPOSED DECAY SCHEME OF Te^{117}

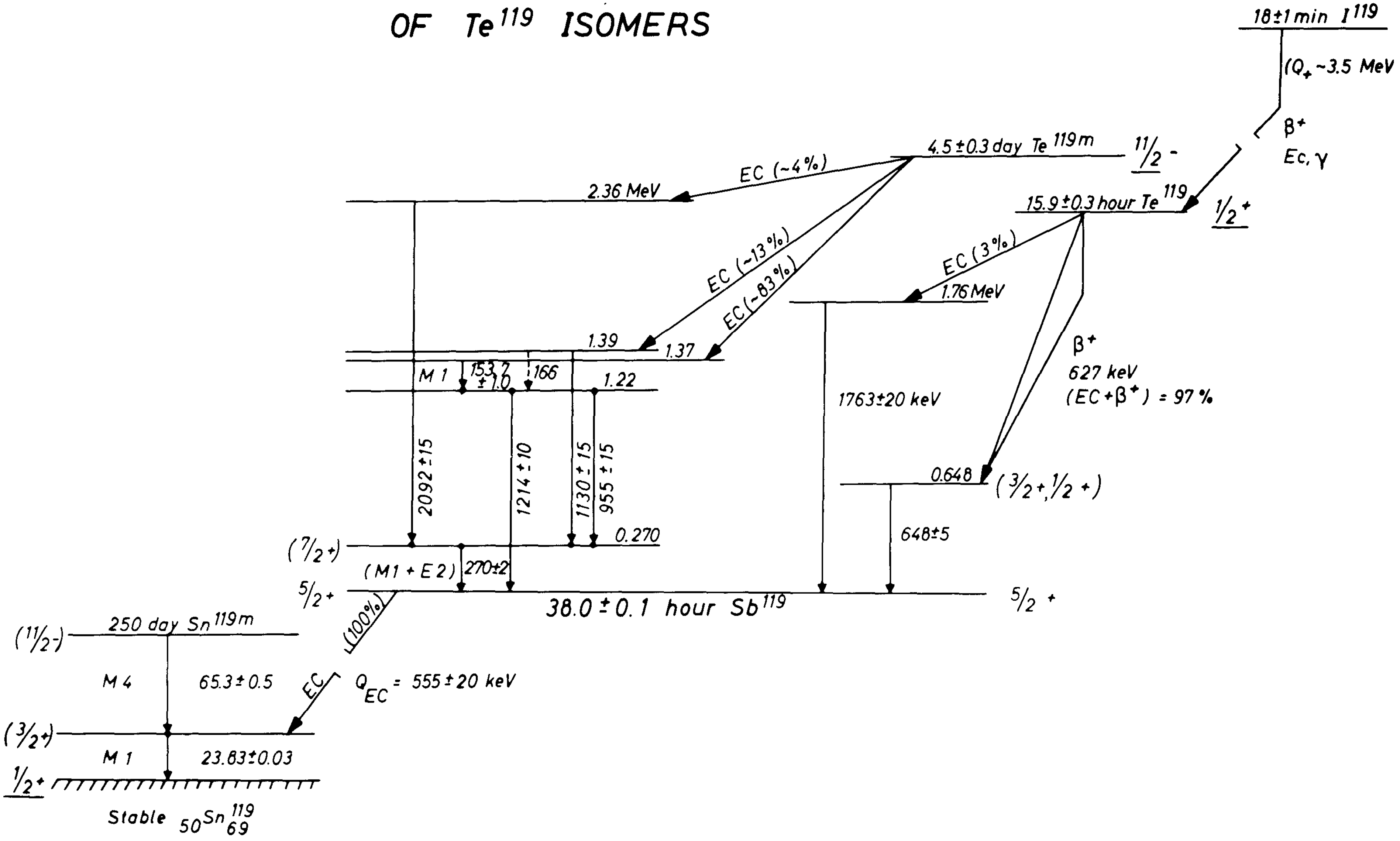


427 59

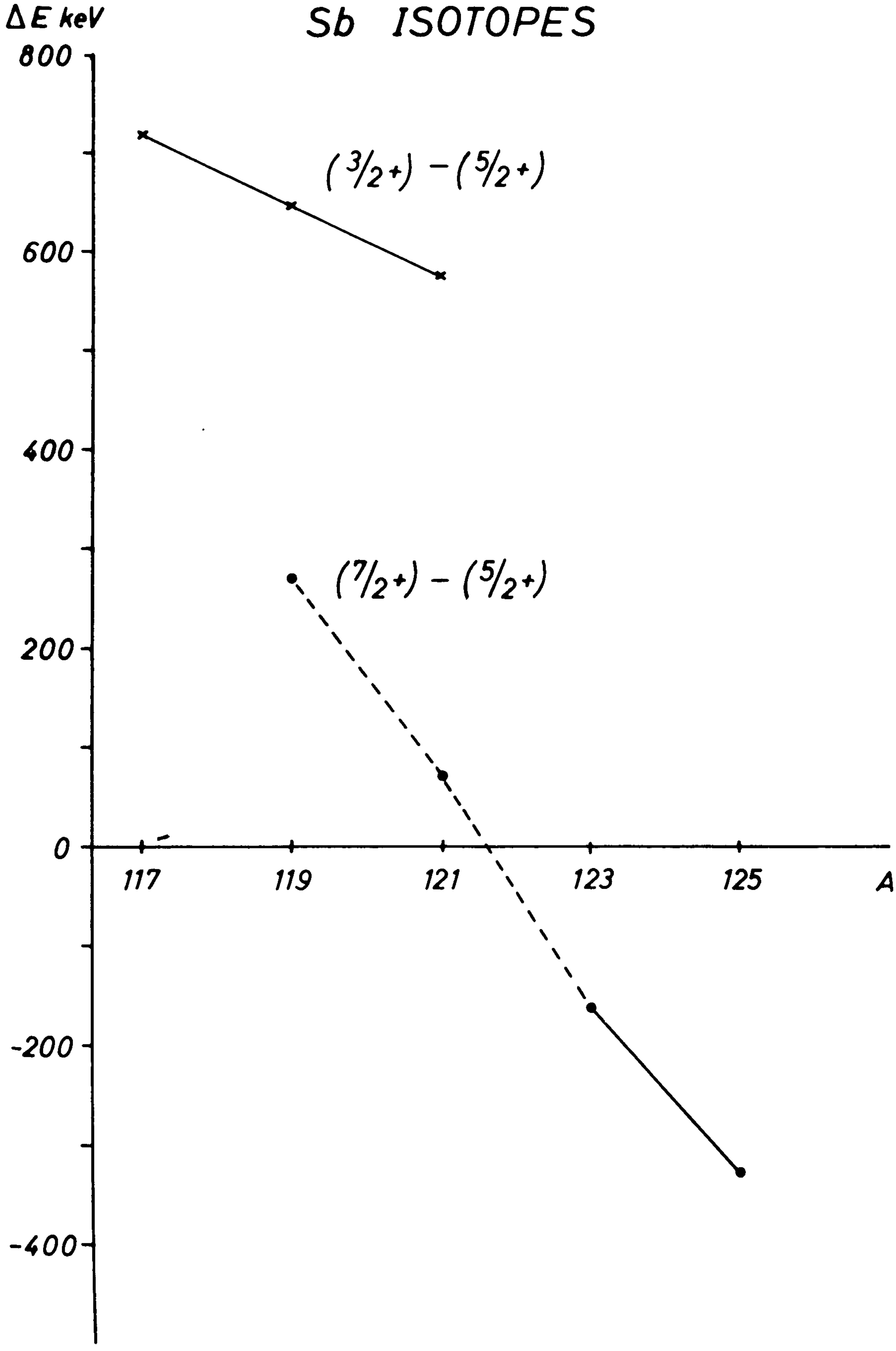
PROPOSED DECAY SCHEME OF Te^{118}



PROPOSED DECAY SCHEME OF Te^{119} ISOMERS



LEVEL SYSTEMATICS IN ODD-A Sb ISOTOPES



APPENDIX III.

A. Poularikas, S. Umemoto, E. Bramlitt and D. G. Gardner

Some Additional (n,He^3) Reactions Induced by 14.8 Mev Neutrons

Submitted for Publication, 1960

Preprint

Some Additional (n,He^3) Reactions Induced By 14.8 Mev Neutrons*

A. Poularikas, S. Umemoto, E. Bramlitt and D. G. Gardner
Department of Chemistry, University of Arkansas
Fayetteville, Arkansas

*Supported in part by the U. S. Atomic Energy Commission

In a previous paper (1) a number of (n,He^3) reaction cross-sections at 14.8 Mev were measured for the first time. In this note we report some additional new (n,He^3) cross-section values and correct one value given in the first paper.

The following isotopes were studied: Mg^{26}, K^{41}, Cu^{65}, As^{75} and Zr^{94}. In the case of Cu^{65} samples enriched to 93% in the isotope were employed in addition to natural copper foil. Chemical separations were employed for the irradiated samples of potassium, arsenic, zirconium and neodymium. The gross beta decay was followed with a 2-π end-window methane flow proportional counter, and the data was corrected for the usual sources of error (2). Identification of the products was accomplished by comparison with the well established half-lives of the nuclides formed in the irradiation. We report the

---

(1) I. Kumabe, A. Poularikas, I. L. Preiss, D. G. Gardner and R. W. Fink, Phys. Rev., <u>117</u>, 1568 (1960).

(2) R. G. Wille and R. W. Fink, Phys. Rev., <u>112</u>, 1950 (1958).

cross-section values as the limits found in analyzing the gross beta decay curves. An external copper monitor foil was used to determine the neutron flux. A cross-section value of 556 mb for the $Cu^{63}(n,2n)Cu^{62}$ reaction was used here.

The results obtained are listed below:

$Cu^{65}(n,He^{3})Co^{63}$, 1.45 hr, 1-3 mb
$Zr^{94}(n,He^{3})Sr^{92}$, 2.7 hr, 0.9-1.0 mb
$Nd^{148}(n,He^{3})Ce^{146}$, 13.5 min, 0.6-0.8 mb
$Mg^{26}(n,He^{3})Ne^{24}$, 3.4 min, < 0.5 mb (not observed)
$K^{41}(n,He^{3})Cl^{39}$, 55.5 min, < 0.2 mb (not observed)
$As^{75}(n,He^{3})Ga^{73}$, 5.1 hr, < 0.5 mb (not observed)

In the case of Zr^{94} a slight correction was made to allow for the presence of some Sr^{87} produced by an (n,α) reaction in Zr^{90}. It was assumed that the latter cross-section was 10 mb and that the efficiency of the counter used in this work for gamma rays was 3%.

The previously reported value (1) for the $As^{75}(n,He^{3})Ga^{73}$ cross-section is in error. In the previous work no chemical separation was employed. In this work gallium was separated by a solvent extraction procedure from the other reaction products. The decay curve of the gallium fraction shows the presence of only one principle activity, the 14.1 hr activity from Ga^{72}. No trace of the 5.1 hr Ga^{73} was observed. The only other activity that could be seen was an 8 minute activity that could have been Ga^{74}.

From the work done so far in this laboratory it would appear that (n,He^3) reactions will be observed only for medium weight nuclei when 14.8 Mev neutrons are used. For the lighter elements the Q values become too large, and for the heavier elements the Coulomb barrier inhibits the process. What is really needed at this point is energy and angular distribution measurements for this type of reaction. The results of these measurements would help shed light on the exact mechanism of this reaction.

APPENDIX IV.

I. Kumabe, A. D. Poularikas, I. L. Preiss,
D. G. Gardner and R. W. Fink

(n,He^3) Reactions of Medium Weight Nuclei Induced by 14.8-Mev Neutrons

see Phys. Rev. 117, 1568 (1960)

~~Reprint~~

APPENDIX V.

D. G. Gardner and L. M. Epstein

Protection Against Radiation Damage in Polymethylmethacrylate by High Energy Electrons and by Ultraviolet Light

J. Chem. Phys.
Accepted for Publication, 1960

Preprint

APPENDIX VI.

I. L. Preiss and R. W. Fink

New Isotopes of Cobalt; Activation Cross-sections of Nickel, Cobalt and Zinc for 14.8 Mev Neutrons

see Nuclear Phys. 15, 326 (1960)

~~Reprint~~

APPENDIX VII.

R. G. Wille and R. W. Fink

Activation Cross-Sections for 14.8-Mev Neutrons and Some New Radioactive Nuclides in the Rare Earth Region

Phys. Rev. 118, 242 (1960)

~~Reprint~~

APPENDIX VIII.

A. Poularikas, J. Cunningham, W. McMillan,
J. McMillan and R. W. Fink

New Isomers of Scandium-50 and Indium-120; Gamma-rays in Lutecium-178 Decay

see J. Inorg. and Nuclear Chem. 15, 196 (1960)

~~Reprint~~

APPENDIX IX.

I. Kumabe and R. W. Fink

The Angular and Energy Distribution of Protons from Ni^{58} Reactions Induced by 14.8 Mev Neutrons

see Nuclear Phys. 15, 316 (1960)

~~Reprint~~

APPENDIX X.

H. M. Schwartz

Ritz-Hylleraas Solutions of the Ground State of Two-Electron Atoms Involving Fractional Powers

see Phys. Rev. 120, 483 (1960)

~~Reprint~~

APPENDIX XI.

C. T. Davis and A. Fry

Oxygen Function Rearrangement in
3,3-Dimethylbutan-2-one-[2-^{14}C]

see Chem. & Ind. (London), 227 (1960)

~~Reprint~~

APPENDIX XII.

A. Fry, M. Eberhardt and I. Ookuni

Acid-Catalyzed Rearrangement of Diethyl Ketone and Diisopropyl Ketone

see J. Org. Chem., 25, 1252 (1960)

~~Reprint~~

APPENDIX XIII.

D. Jeffrey

The Kinetics of Oxygen Exchange of Substituted Benzyl Alcohols as a Function of Acidity

Ph.D. Dissertation Abstract
University of Arkansas, 1961

THE KINETICS OF OXYGEN-18 EXCHANGE OF SUBSTITUTED BENZYL ALCOHOLS AS A FUNCTION OF ACIDITY

Abstract of thesis submitted in partial fulfillment
of the requirements for the degree of
Doctor of Philosophy

By

DAVID AUSTIN JEFFREY
(B.Sc., Acadia University, 1952)
(M.S., University of Arkansas, 1957)

1961
The University of Arkansas

The Kinetics of Oxygen-18 Exchange of Substituted Benzyl Alcohols as a Function of Acidity

ABSTRACT

Reactions involving the benzyl system are frequenctly considered to lie in the borderline region between the pure S_N1 and S_N2 mechanistic classifications (1). One of the important methods which has been used to gain information about these borderline reactions is to study the effect of changing a ring substituent on the rate of a chemical reaction (1). In an ideal case a given reaction might be shifted from the S_N1 extreme to the S_N2 extreme simply by changing the ring substituent from p-methoxy to p-nitro. The acid-catalyzed exchange of water with substituted benzyl alcohols is a very desirable reaction to study in this respect since the ideal S_N2 transition state or intermediate would be completely symmetrical.

Furthermore, to the extent that the Zucker-Hammett hypothesis (2) is valid, study of the exchange reactions as a function of acidity should provide a clear cut distinction between an S_N1 (A-1) case and an S_N2 (A-2) case. According to this hypothesis, an A-1 reaction will be characterized by a linear relationship between $-H_o$ and log k_1 whereas an A-2 reaction will show a linear relationship between log C_{H^+} and log k_1.

Accordingly, the rates of exchange of oxygen-18 enriched unsubstituted, p-methoxy-, p-methyl-, p-chloro- and p-nitrobenzyl alcohols with

water were measured as a function of the sulphuric acid concentration of the reaction medium. It was later found that the rate of exchange of the oxygen-18 enriched p-nitrobenzyl alcohol was inconveniently slow compared with that of the other compounds, and as a result, a detailed kinetic study was not made.

In each case exchange studies were made at two different temperatures for 0.5 M sulphuric acid and the results were used in calculating the Arrhenius activation energy and entropy of activation. The results of these calculations are shown in Table I.

Table I

Values of E and ΔS at 25° for the Acid-Catalyzed Oxygen Exchange of Benzyl Alcohols

Alcohol	$k_{ex} \times 10^8$ at 25° (sec^{-1})	E (kcal/mole)	ΔS	$k_{ex} \times 10^5$ at 100° (sec^{-1})
Anisyl	12,200	22.0	-5.2	21,000
p-Methylbenzyl	47.6	24.5	-6.8	171
Benzyl	5.61	25.8	-7.1	3.62
p-Chlorobenzyl	2.43	26.0	-8.2	1.66

The data in Table I show that the relative rates of the acid-catalyzed oxygen exchange of para-substituted benzyl alcohols is in the following order: $CH_3O > CH_3 > H > Cl > NO_2$. In view of the fact that the electron-donating groups in the para position have an accelerating influence on the rate one may conclude that the benzyl carbon is more positive in the transition state than in the reactant alcohol. Further, the rate of exchange is proportional to h_o (over the range of acidities studied) for each of the above compounds, which shows clearly that the conjugate acid of the alcohol is the reacting species. Thus, to the extent that the Zucker-Hammett hypothesis is valid, all of these compounds react by an A-1 mechanism.

However, the entropy of activation data above suggest that the exchange reaction becomes increasingly more S_N2 like as the electron donating power of the substituent decreases (3,4). Further, the observed positive curvature of a Hammett sigma-rho plot of the data suggests that the reaction is taking on increasing A-2 (S_N2) character as the electron-donating power of the substituent increases, which may be indicative of a unity of mechanism for this particular reaction as has been proposed by Swain and Landsdorf (1) for the reactions of substituted benzyl alcohols.

An alternate expression of the relationship between rate constant and acidity for the A-2 type reaction is

$$\log k/a_{H_2O} = -H_o + \log \frac{f_s\, f_{BH}}{f_{\ddagger} f_B} + \text{constant}$$

and it is proposed that the linearity of a plot of log k/a_{H_2O} versus $-H_o$ is more clearly diagnostic of the A-2 mechanism than is the supposed linearity of a plot of log k versus log C_{H^+}. Examples from the literature in support of this idea have been presented since the acidity range (0.1 to 2.0 M) used in this work was not sufficiently wide to provide an adequate test.

References

1. C. G. Swain and W. P. Landsdorf, J. Am. Chem. Soc., 73, 2813 (1951).
2. For a review of this subject see F. A. Long and M. A. Paul, Chem. Revs., 57, 935 (1957).
3. V. Gold and J. Hilton, J. Chem. Soc., 843 (1955).
4. F. A. Long, J. G. Pritchard and F. S. Stafford, J. Am. Chem. Soc., 79, 2362 (1957).

APPENDIX XIV.

J. Hill

Chlorine Isotope Effects in the Reactions of Benzyl and Substituted Benzyl Chlorides with Various Nucleophiles

Ph.D. Dissertation Abstract
University of Arkansas, 1961

CHLORINE ISOTOPE EFFECTS IN THE REACTIONS OF BENZYL AND SUBSTITUTED BENZYL CHLORIDES WITH VARIOUS NUCLEOPHILES

Abstract of thesis submitted in partial fulfillment
of the requirements for the degree of
Doctor of Philosophy

By

JOHN WILLIAM HILL
(B. S., Middle Tennessee State College, 1957)

1961
The University of Arkansas

ABSTRACT

The justifiability of classifying nucleophilic displacement reactions into the mechanistic categories S_N1 and S_N2 has been the center of a great deal of controversy. The debate centers about the role of solvents in these reactions. The reactions of benzyl halides are known to be "borderline" between the two mechanistic categories. It was hoped that kinetic isotope effect studies of the displacement reactions of a series of substituted benzyl chlorides would yield more information about the intimate details of the displacement process and would thus help in deciding on questions of classification. The reactions of p-methoxy-, p-methyl-, unsubstituted, p-chloro-, and p-nitrobenzyl chlorides with each of three nucleophiles in 80 percent aqueous dioxane at 30° have been studied and are reported here. The nucleophiles employed were water, cyanide ions, and thiosulfate ions.

The hydrolysis of each of the benzyl chlorides was found to exhibit good first order kinetics. The reactions of p-methoxy- and p-methylbenzyl chlorides with potassium cyanide and that of p-methoxybenzyl chloride with sodium thiosulfate were also kinetically first order. On the other hand, the reactions of p-nitro- and p-chlorobenzyl chlorides with sodium thiosulfate and that of the p-nitro compound with potassium cyanide displayed second order

27 34

kinetics. The remaining reactions, viz., those of the unsubstituted and p-chlorobenzyl chlorides with potassium cyanide and of unsubstituted and p-methylbenzyl chlorides with sodium thiosulfate, seemed to exhibit mixed order kinetics.

A good qualitative correlation was found to exist between the kinetic order of a given reaction and the magnitude of the kinetic isotope effect observed for that reaction. Those reactions exhibiting first order kinetics gave isotope effects (k^{35}/k^{37}) of approximately 1.0073, while those which were kinetically second order exhibited isotope effects close to 1.0054. Those reactions which displayed mixed order kinetics gave isotope effects intermediate in magnitude between the above values.

The hydrolysis of benzyl chloride at 50°, that of p-nitrobenzyl chloride at 90°, and the reaction of the latter with potassium cyanide at 50° were also studied. The isotope effects observed for these reactions were the same as those observed for the corresponding reactions at 30°. Hence, there is little or no temperature dependence for the kinetic isotope effects over this range.

Attempts to correlate the observed isotope effects with theory were not very fruitful. The Bigeleisen equation predicts isotope effects of far greater magnitude than those observed, but it does predict a trend in magnitude in the same direction as that observed. The lack of temperature dependence which was observed is not satisfactorily explained even with the invocation of complications of the model ordinarily used for isotope effect calculations. However, it appears that the magnitude of the observed kinetic isotope effect may be used on an empirical basis as a mechanistic criterion.