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THE USE OF PULSE RADIOLYSIS TO STUDY TRANSIENT SPECIES IN THE GAS PHASE¹

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ABSTRACT

Examples are chosen from the literature to show the types of species which have been investigated in the gas phase using the pulse radiolysis technique. The types of processes occurring in pure rare gases and rare gases containing additives are examined. Techniques used to study ion-recombination processes, ion-molecule reactions, and electron capture reactions are discussed and examples of typical results are given. The use of pulse radiolysis to determine rate constants for reactions of atoms and free radicals is also examined.

1. INTRODUCTION

Since the introduction of the technique of pulse radiolysis in 1960 (1) and its subsequent application to gases, a wide variety of species and reactions have been investigated using this technique. The area of gas-phase pulse-radiolysis has been the subject of two reviews (2,3). In some instances a pulse of ionizing radiation is used to create (via ion-recombination and other mechanisms) neutral reactive species in a manner which is often more convenient than other techniques (photochemical, thermal). In other instances, the charged species are studied (ion-recombination, ion-molecule reactions, electron capture).

An understanding of the ways in which pulses of ionizing radiation can be used in studying gas phase processes depends to some extent on an understanding of the time scale of various processes. This time scale is depicted in Figure 1, which shows the primary

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Figure 1. Approximate time scale of events in gas phase pulse radiolysis.

species produced by a pulse (time = 0) as being electrons, ions (which are, in general, excited), and neutral excited states. Light emission from excited species is, in general, observed in the range 10^{-9} to 10^{-7} sec and is in competition with other processes, e.g., fragmentation, ion-molecule reactions, and energy transfer. Kinetic information on these processes can be obtained via observation of the time dependence of the light emission.

Electron thermalization takes place in the 10^{-9} to 10^{-7} sec regime, as do ion-molecule reactions. "Recombination" reactions among oppositely charged species takes place over 10^{-9} to 10^{-6} sec, dependent, of course, on the concentration of ions produced by the pulse. These ion-recombination reactions produce atoms, radicals, and excited states. "Delayed" light emission as a result of the excited states can be observed and used to obtain information on ion-recombination rates.

Transfer of excitation energy can result in delayed production of ions, as well as light emission due to excitation of minor constituents.

In most cases ionic species have undergone recombination by 10^{-6} to 10^{-5} sec and neutral atoms and free radicals are the predominant transient species. These combine with one another to form stable molecules on a 10^{-5} to 10^{-2} sec time scale; note, however, that transformations by reaction with substrate molecules are possible on the same time scale in the case of more reactive species such as H or OH. Less reactive radicals such as CH_3 , NH_2 , or HO_2 generally do not react with substrate molecules (at room temperature) in less than 10^{-1} sec, and can therefore be assumed to react only by radical combination reactions.

In this presentation, examples will be given of gas-phase processes which have been investigated by pulse-radiolysis.

No attempt will be made to cover all of the work done on gas-phase pulse-radiolysis, and the work discussed will be chosen to some extent on the basis of its familiarity to the author.

Obviously, suitable detection methods are quite important; however, the detection methods will not be discussed in detail, because other chapters in this book deal with that subject.

2. EXCITED STATES

Excited state formation and decay processes have been investigated by following both light emission and optical absorption. Examples will be chosen from the large number of papers published to show the types of phenomena encountered.

Figure 2. Grotrian diagram (2) of the 1s and 2p levels of Ar (not to scale).

2.1. Pure Rare Gases

In pure rare gases, emissions and absorptions have been studied (4-8) which originate from the Paschen 1s (the four lowest energy excited states) and 2p (the next 10 excited states) atomic levels, shown schematically in the Grotrian diagram in Figure 2. Absorptions and emissions due to rare gas dimer species have also been studied (4,9,10).

Of the four 1s excited states, the $1p_1$ and $3p_1$ are resonance states, and the corresponding transitions to the ground state can be observed in the vacuum u.v. The $3p_0$ and $3p_2$ are metastable states. All four states can be observed in absorption, corresponding to transitions to the 2p states. The 2p levels can be followed by observing their transitions to 1s levels via the resulting light emission in the visible and near i.r. regions. Rare gas dimer species have been directly observed by their absorptions in the i.r. region.

Figure 3. Emission and absorption in Ar.

The general picture which has emerged from the experimental results is that the $1s$ levels are mainly populated by processes occurring after energy has been imparted to the gas by the pulse. For example, Figure 3 shows the emission and absorption at 842 nm ($1s_4-2p_8$) in about 200 torr argon (4). The results indicate that most of the $1s_4$ state is formed during the decay of the $2p_8$ level. The $1s$ levels are found to be relatively long-lived; the resonance levels have their effective lifetimes extended due to radiation imprisonment.

To continue with the general picture, the situation with respect to the $2p$ levels has been examined with time resolution of several nanoseconds (5). Two mechanisms of production of the $2p$ states are evident, as is depicted in Figure 4. The second peak in Figure 4, which is common to all of the $2p$ levels observed, can be shown to be due to production of the $2p$ level by ion-recombination. This conclusion is based on the observations (5) that decreasing the dose per pulse shifts the peak to longer times (Figure 5), and that it can be entirely eliminated by addition of a small amount of SF_6 , which is an efficient electron scavenger.

Figure 4. Emission at 725 nm in 840 torr Ne using a 5 ns pulse from a Febetron 706.

Figure 5. Emission from 840 torr Ne; $2p_1 \rightarrow 1s_2$ (585 nm). The fast component of the emission is not shown.

The first peak in Figure 4 is due to direct excitation of the rare gas to the 2p level, or to direct excitation of the rare gas to some energy level higher than the 2p level in question followed by a rapid transition. By using low dose per pulse, the two peaks in Figure 4 can be well separated, and results have been obtained on the pressure dependences of the formation and decay kinetics of the first peak. Examples of these results, which were obtained

using a 30 ps linac pulse and a crossed-field photomultiplier (ca 150 ps rise-time), are shown in Figures 6 and 7 for neon (11).

Observation of all of the 2p levels was not possible, but Ar, Kr, and Xe do not show the same pattern as seen in Figures 6 and 7 for Ne. A general trend for the four rare gases is that decay rates become greater with increasing rare gas pressure. These results have not been completely interpreted; however, the variation of integrated emission with pressure suggests that the faster decay rates at higher pressure are not a result of removal of the 2p levels by dimer formation. That is, higher pressure seems simply to accelerate the emission to the 1s levels. This is in agreement with the results of Firestone and co-workers, who report that the observed initial (i.e., at times where all 2p has gone to 1s) concentrations of the 1s₂ and 1s₄ states are directly proportional to pressure, which indicates that the faster decay of the 2p levels does not prevent the 1s levels from being populated in proportion to the dose absorbed per unit volume, which is proportional to the pressure.

To complete the general picture on the pure rare gas systems, the work of Firestone and co-workers on the decay of the 1s levels and the formation of excited dimers will be summarized. The mechanism proposed (9) in the case of the 1s resonance levels of argon is shown below.

The species $\text{Ar}_2^*(v)$ is vibrationally excited. The lowest lying metastable rare gas eximer states, e.g., Ar_2^* in reactions (3) and (4), are proposed to decay by radiative processes, e.g.,

with emission in the vacuum u.v.

Reactions (1)-(4) provide an explanation for the pressure dependences of the observed (7) first-order decays of the 1s₂ and 1s₄ levels of Ar shown in Figure 8, where the observed rate constant, k_{obs} , is defined by equation 1.

Figure 6. Emission from 2p levels of Ne following a 30 ps pulse.

Figure 7. Pressure dependence of emission from the $2p_7$ level of Ne following a 30 ps pulse.

Figure 8. Pressure dependences of the observed pseudo-first-order disappearance rates of the $1s_2$ and $1s_4$ states of Ar. The curves result from equation I.

$$k_{\text{obs}} = \frac{\frac{k_1 k_3}{k_2 + k_4} [\text{Ar}]^2 + \frac{k_1 k_4}{k_2 + k_4} [\text{Ar}]}{1 + \frac{k_1 + k_3}{k_2 + k_4} [\text{Ar}]} \quad (\text{I})$$

Because of the large value of k_2 the denominator can be set equal to unity.

The decay of the relatively long lived metastable dimer species, e.g., reaction (5), which results from reaction (1) has been thoroughly investigated and found to proceed only by the radiative process indicated (9). The radiative decay constants for $\text{Ne}_2(^3\Sigma_u^+)$, $\text{Ar}_2(^3\Sigma_u^+)$, and $\text{Kr}_2(^3\Sigma_u^+)$ are $1.51 \pm (0.03) \times 10^5$, $3.10 \pm (0.04) \times 10^5$, and $2.83 \pm (0.08) \times 10^6$ sec $^{-1}$, respectively (9). It is important to note that at low rare gas pressure the radiative decay of these dimers becomes faster than their formation rate by reactions (1)-(4) and the observed decay rate of the absorption due to the dimers therefore becomes slower than the radiative decay rate (9). As shown in Figure 9, the observed decay constant reaches a plateau value equal to the radiative constant, at sufficiently high pressure.

Figure 9. Pressure dependence of the decay constant of the rate limiting slow step in the decay of $\text{Ar}_2(^3\Sigma_u^+)$.

2.2. Rare Gases Containing Additives

Only a few of the many papers on this subject will be discussed. Particular attention will be paid to illustrating the variety of mechanisms by which excited states are produced by reactions involving the additives. Numerous measurements of quenching rate constants for various additives reacting with excited states have been made but these will not be discussed here.

A system which, despite its simplicity, has revealed a wealth of interesting (but complex) data on light emission is Ar-I_2 . Detailed observations (12,13), from less than a nanosecond to several microseconds, in the u.v. and visible regions, have shown that the observed spectral peaks correspond to known states of molecular iodine. The spectrum is shown in Figure 10.

Only the strongest emission ($\approx 342 \text{ nm}$) could be examined with sub-nanosecond time resolution (13). The emission at 342 nm exhibits a rather complex behavior, as shown in Figures 11 and 12. The "fast" peak shown in Figure 11 is also present in the cases of the 4 and 40 ns pulses (Figure 12), but is offscale and is not shown. The important experimental fact is that there appear to be

Figure 10. Emission spectrum (uncorrected) in the Ar-I₂ system observed about 10 ns after a 40 ns pulse.

Figure 11. Emission at 342 nm following a 30 ps pulse in the Ar-I₂ system.

three processes leading to the emission at 342 nm (corresponding to the peaks A, B, and C in Figures 11 and 12).

Figure 12. Emission at 342 nm following 4 ns and 40 ns pulses. Zero time corresponds to the pulse mid-point, and the results are normalized to the same maximum.

The processes responsible for peak A are proposed (13) to be:

⋮
etc.
⋮

This mechanism is based on variations in the emission kinetics with change in wavelength (320-342 nm region) and pressure, the results of which show that the emission at the low wavelength end of the band forms and decays while the 342 emission is forming. This suggests a vibrational deactivation sequence as shown in reactions (7)-(10); the effects of pressure also support the idea of a vibrational deactivation sequence.

Figures 11 and 12 show that the "fast" 342 nm emission decays, but that the light intensity subsequently reaches a second maximum. Results with a 4 ns pulse of somewhat higher dose than the 30 ps pulse used in Figure 11 suggest an additional third emission maximum (C), as shown in Figure 12. Using a 40 ns pulse (about 10 times the dose of the 4 ns pulse) apparently causes B and C to merge. When a small amount of SF₆, an efficient electron scavenger, is added, peak C is eliminated, but A and B are still observed. Thus, B is thought to arise from reactions initiated by excited Ar produced by direct excitation. A detailed analysis of the results (12) suggests $\text{Ar}^* + \text{I}_2 \rightarrow \text{I}^* + \text{I}_2$ followed by $\text{I}^* + \text{I}_2 \rightarrow \text{I}_2^*$. Peak C is thought to arise from several ionic reactions which eventually result in I_2^* .

An interesting observation concerning this system is that the emission decays shown in Figure 12 follow pseudo-first-order kinetics from 300 to 900 ns, i.e., over several half-lives. This is unusual in view of the ionic processes, which would be expected to result in a second-order component. This finding requires that one of the ionic species must react by a first order reaction to produce an ion which doesn't result in eventual production of I_2^* . A kinetic scheme incorporating such a reaction has been found to give reasonable agreement with the experimental results (12).

A similar situation exists with the emission at 342 nm in Xe, I₂ mixtures (14). However, in this case stronger emissions in the region of 253 and 319 nm are observed, and have been ascribed to $\text{XeI}^*[\text{B}(1/2)]$ (15). Analysis of the variation of emission kinetics with wavelength and pressure indicates that, somewhat surprisingly, the XeI^* is formed by reactions of excited I₂ with Xe, the excited I₂ being formed by direct excitation. As in the case of the Ar, I₂ system, there is strong evidence of a vibrational deactivation sequence. The observations are summarized in Figures 13 and 14.

Using longer pulses (higher dose per pulse) shows that a slower sequence of reactions occurs, involving ionic precursors, which produces the same excited states (14).

The formation of $\text{XeI}^*[\text{B}(1/2)]$ is observed also in pulse radiolysis (using 15 ns pulses) of Xe, CF₃I mixtures (15), but in contrast to the Xe, I₂ system XeI^* is formed by the reaction of Xe^* (or Xe_2^+) with CF₃I, e.g.,

An ionic component to XeI^* formation is also observed in this system when the CF₃I pressure is small enough that Xe_2^+ reacts with I⁻ (to give XeI^*) rather than with CF₃I.

Figure 13. Dependence of the emission vs time profile on wavelength in the Xe- I_2 system (14).

Figure 14. Effect of Xe pressure on the time dependence of emission at 280 nm in the Xe- I_2 system (14).

3. CHARGED SPECIES

3.1. Recombination

An early example of the use of pulse-radiolysis to study ion-recombination involved the measurement of light emission from N_2 irradiated with pulses of about 10-40 ns duration from a linear accelerator (16). Emission from the $C^3\pi_u$ state of N_2 was observed to follow kinetics indicating that this state was produced in the reaction

The emission decayed over a time period much longer than the lifetime of the $C^3\pi_u$ state. Therefore, assuming that $[e^-] = [N_4^+]$, or that other positive ions react with e^- with the same rate constant as k_{12} , one can easily see that $(\text{Emission Intensity})^{1/2}$ should be proportional to $[e^-]$. Plots of $(\text{Emission Intensity})^{1/2}$ vs time were linear, verifying the second-order nature of the reaction. Using appropriate chemical dosimetry, $(\text{Emission Intensity})^{1/2}$ was converted to electron concentration; second order plots of $[e^-]^{-1}$

Figure 15. Second order plots of electron-ion-recombination in N_2 , determined by observation of emission from $N_2(C^3\pi_u)$.

vs time are shown in Figure 15 for three pulse sizes. The value of k_{12} obtained was $3.0 \times 10^{-6} \text{ cm}^3 \text{ s}^{-1}$, with no effect of pressure between 280 and 980 torr, and $T^{-1/2}$ dependence from 25 to 205°C.

Ion-recombination reactions have also been studied by following light emission from naphthalene or anthracene excited singlet states in the vapor phase (17), but methods in which the disappearance of charge is measured directly are more general. Armstrong and co-workers have used both steady-state and pulsed irradiation methods to measure recombination coefficients in a variety of gases, i.e., NH_3 , H_2O , CO_2 , and others. Their charge collection methods use relatively weak intensities of x-rays, either pulsed or continuous, producing ion concentrations in the range of 10^8 cm^{-3} (18). Gases are irradiated in ionization chambers, and absolute measurements of charge collected are made with (1) continuous radiation and pulsed high voltage for charge collection, and (2) pulsed irradiation and pulsed high voltage for charge collection. In (1), the time between collection pulses is great enough for the steady-state ion concentration to be reached. The high voltage pulse is made long enough that all steady-state ions are collected. This situation is depicted in Figure 16. From the rate of ion collection as a function of the length of the high voltage pulse, the steady-state ion concentration, n_{ss} , and the rate of ion production, R , can be determined. These values allow the recombination coefficient, α , to be determined, because $\alpha = R/n_{ss}^2$.

In (2) an x-ray pulse in the tens of msec range (long enough for the ion concentration to reach steady state during the pulse) is used, and a high voltage collecting pulse is applied for a variable time in a manner which enables the steady-state ion

Figure 16. Schematic representation of the pulsed collection, continuous irradiation method used in measuring ion-recombination rates (18).

Figure 17. Depiction of the pulsed-irradiation, pulsed charge collection method used in measuring ion-recombination rates (18).

concentration during the pulse and the concentration as a function of time after the pulse to be measured. This technique is illustrated in Figure 17. Variation of the high-voltage pulse length, Δt_1 , keeping t_0 fixed, allows determination of the steady state ion concentration reached during the pulse as well as R , the rate of ion formation by the pulse. Applying the high-voltage pulse Δt_2 at t_2 allows determination of the ion concentration at t_2 to be determined. The recombination coefficient can be determined from the steady state ion-concentration and R or from the curve formed by varying t_2 .

Another method of determining recombination coefficients uses a microwave absorption technique to study electron decay following a pulse (19). The gas is irradiated in a cell consisting essentially of a piece of x-band waveguide. The change in microwave conductivity can be used to calculate in a straightforward manner the concentration of electrons if the mobility of the electron is known.

One of the interesting results of these recombination studies is the information obtained on the effect of pressure on recombination (18,19). Figures 18 and 19 illustrate the results for NH_3 . The electron-ion recombination coefficient is found (19) to follow equation II.

Figure 18. Ion-ion recombination coefficients in ammonia, nitrous oxide systems vs ammonia pressure (18).

Figure 19. Electron-ion recombination coefficients in ammonia as a function of ammonia pressure. The circles are from reference 18 and the +'s are from reference 19.

$$\alpha = \alpha_2 + \alpha_3 N, \quad (\text{II})$$

(where α_2 is the zero pressure extrapolated limit and N is the gas concentration) up to the pressures indicated in Table I. Such data are of considerable value in providing tests of theories of recombination.

Table I. Electron-Ion Recombination Coefficients (19).

Gas	$10^6 \times \alpha_2$ ($\text{cm}^3 \text{ s}^{-1}$)	$10^{25} \times \alpha_3$ ($\text{cm}^6 \text{ s}^{-1}$)	Pressure Limit (torr)
H_2O	4.1	270	20
NH_3	5.6	69	100
$(\text{CH}_3)_2\text{CO}$	6.4	55	100
CH_3Cl	7.1	26	100
CO_2	3.7	5.8	700
$(\text{CH}_3)_4\text{C}$	7.0	2.5	700

It should be noted that the identity of the recombining ions in such studies is affected by clustering. Progress has been made in understanding the effects of clustering on recombination in ammonia and water vapor (20).

3.2. Ion-molecule Reactions

An excellent example of the application of pulse-radiolysis techniques to measurement of ion-molecule reaction rates involves the reaction of N_2^+ ($X^2\Sigma_g^+$, $v=0$), the ground state of N_2^+ , with various compounds (21). The absorption to the $\text{N}_2^+(\text{B}^2\Sigma_u^+, v=0)$ state at 391.44 nm was monitored. A pulse from a Febetron 706 produced a sufficiently high concentration of N_2^+ , and in 40 torr N_2 , the reaction $\text{N}_2^+ + 2\text{N}_2 \rightarrow \text{products}$ was determined to account for the observed 19 ns half-life of the absorption. Other compounds were added in smaller concentrations, and rate constants for reaction with $\text{N}_2^+(\text{X}^2\Sigma_g^+, v=0)$ were obtained. These measurements are summarized in Table II.

Table II. Rate Constants for Reactions of N_2^+ ($X^2\Sigma_g^+$, $v=0$) (21).

Reactant	Rate Constant ($\text{cm}^3 \text{s}^{-1}$) $\times 10^{10}$	Reactant	Rate Constant ($\text{cm}^3 \text{s}^{-1}$) $\times 10^{10}$
O_2	< 0.4	Cyclopropane	15 ± 0.4
Xe	0.86 ± 0.12	SF_6	15 ± 1.3
CO	1.1 ± 0.3	H_2	19 ± 3.8
NO	4.1 ± 0.5	NH_3	18 ± 3.6
C_2H_2	8.8 ± 0.8	H_2O	23 ± 3.6
CH_4	10.0 ± 1.6		

3.3. Electron Capture

The microwave conductivity method coupled with pulse-radiolysis has provided great detail on electron capture rate constants. The method is very sensitive and concentrations of $\sim 10^7$ electrons per cm^3 can be used; therefore, low intensity (e.g., a Febetron 706 pulse can be converted to x-rays) can be used and interference from recombination reactions can be ignored. A "representative" sample of rate constants determined by this method taken from a review (3) is given in Table III.

Table III. Electron Capture Rate Constants at 25°C

Reactant	Rate Constant ($\text{cm}^3 \text{s}^{-1}$)	Reactant	Rate Constant ($\text{cm}^3 \text{s}^{-1}$)
CCl_4	4.2×10^{-7}	CH_3Br	7.0×10^{-12}
SF_6	2.2×10^{-7}	C_2H_5Br	2.8×10^{-13}
$c-C_4F_6$	1.4×10^{-7}	$c-C_3F_6$	$< 3 \times 10^{-14}$
$c-C_4F_8$	1.2×10^{-8}	CH_2F_2	1.6×10^{-14}
C_3F_6	3.0×10^{-10}	CH_3Cl	$< 2 \times 10^{-15}$
$n-C_4F_{10}$	1.0×10^{-11}	CF_4	$< 1 \times 10^{-16}$

An example of the precision and detail available using the microwave conductivity technique is the work done recently on electron attachment to O_2 , and the effects of various added compounds on the process (22-26). In general, the mechanism has been shown to involve the following four reactions as the primary mechanism (Bloch-Bradbury mechanism):

With $M = H_2$ or D_2 , this mechanism was found to be satisfactory, but with $M = N_2$, anomalous effects of pressure were observed which were explained by the following additional reactions:

In other words, a four-body component was needed in the reaction scheme to explain the observed effects of pressure. In detail, reactions (13)-(16) yield equation III

$$\tau P_{O_2} = \frac{1}{k_{13}} + \frac{k_{14}/k_{13}}{rk_{15} + k_{16}} \times \frac{1}{P_{N_2}}, \quad (III)$$

where τ is the observed electron lifetime and $r = P_{O_2}/P_{N_2}$. At constant r , it was observed that plots of τP_{O_2} vs $1/P_{N_2}$ gave negative intercepts. Inclusion of reactions (17)-(20) allowed this discrepancy to be explained. The results indicated that reaction (19) is two orders of magnitude faster than reaction (20).

In addition to this "four-body" mechanism, experiments with various hydrocarbons as third bodies have been interpreted as indicating the importance of electron attachment to pre-existing van der Waals molecules ($O_2 \cdot M$). In essence, the existence of these molecules shows up as deviations from the behavior predicted by

reactions (13)-(16), i.e., at high P_M anomalously high rates are observed. The four-body mechanism is not appropriate because it predicts that the observed effective (pseudo-first-order) rate constant cannot be greater than k_{13} , whereas, experimentally several cases show effective rate constants greater than k_{13} .

4. ATOMS AND RADICALS

Studies of atoms and radicals by pulse radiolysis have generally been done to determine spectra and rate constants. The work reported has been done predominantly with the high dose pulse from Febetrons. The high concentration of radicals produced is convenient in terms of the optical absorption techniques usually used, i.e., concentrations in the range 10^{14} - 10^{15} radicals per cm^3 are needed to obtain reasonable signal-to-noise without use of signal averaging.

Many atomic and radical reactions have been investigated by following the absorption of either a reactant or a product. Among the species whose reactions have been studied are OH, H, O, HO_2 , CH, NH_2 , NH, NO_2 , and CN. As an example of this type of study, we will consider some reactions of the HO_2 radical in the following.

The HO_2 radical has a broad absorption spectrum which does not appear to change when H_2O or NH_3 are present (27-29), despite the fact that these substances form complexes with HO_2 , as will be discussed below.

The HO_2 radical is conveniently prepared by pulse-radiolysis of 1200 torr H_2 containing about 5 torr O_2 . Using a Febetron 705 (~ 50 nsec pulse), about 1×10^{15} H atoms per cm^3 are formed by direct excitation of H_2 and ion-recombination, which is over within about a microsecond. The reaction of H with O_2 is a three body reaction, which under the above conditions is complete within ~ 10 μsec . The subsequent reactions of HO_2 occur on a slower time scale; the second-order decay of HO_2 proceeds with an initial $t_{1/2}$ of about 400 μsec under the above conditions.

A typical set of data on HO_2 is shown in Figure 20. The "white" curve through the data represents a second-order "best fit" obtained by computer analysis.

Using the known absorption coefficient of HO_2 at 230 nm, data such as these have been analyzed to determine the Arrhenius parameters for the overall reaction

Figure 20. HO_2 formation and decay observed using a 50 ns pulse from a Febetron 705.

The result obtained is $k_{21} = (1.14 \pm 0.16) \times 10^{-13} \exp(2100 \pm 90/RT) \text{ cm}^3 \text{ s}^{-1}$. The negative activation energy was explained (30) on the basis of an unstable intermediate, H_2O_4 , the overall reaction being in detail

The rate constant for decay of HO_2 was observed to be markedly accelerated when either H_2O or NH_3 was added to the H_2O_2 mixture. (Second-order kinetics were still followed, however.) This effect is shown in Figure 21 for the case of added NH_3 , at several temperatures. The results in Figure 21 were explained on the basis of the formation of a hydrogen bonded complex between HO_2 and NH_3 . It is of interest to note that the absorption spectrum in the 230 nm region does not change appreciably when the complex is formed.

The increase in k_{21} with increasing $[\text{NH}_3]$ requires that the HO_2 complex is more reactive than HO_2 itself, i.e., $k_{25} > k_{21}$.

Figure 21. Rate constant for the HO_2 self-reaction as a function of NH_3 concentration and temperature (k_{obs} is the observed overall rate constant, defined by equation IV).

The results also require that $k_{26} < k_{25}$.

The curves through the data points are the results of a detailed analysis (29) in terms of the reactions given above and the equilibrium

The observed rate constant, k_{obs} , can be shown to be given by equation IV

$$k_{\text{obs}} = \frac{k_{21} + k_{25}K[\text{NH}_3] + k_{26}K^2[\text{NH}_3]^2}{(1 + K[\text{NH}_3])^2}, \quad (IV)$$

where K is k_{27}/k_{28} . The results of the analysis yield the following information. The value of k_{25} is about 9 times k_{21} , whereas k_{26} is only about 3 times k_{21} . The analysis also yields $\Delta H_{298}^\circ = -13 \pm 1.5$ kcal/mol and $\Delta G^\circ = -3.3 \pm 0.2$ kcal/mol for the formation of the complex, i.e., reaction (27).

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