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Doc/EX/13373--73

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OCT 26 1993
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THE COMBINATION REACTION OF CH_3 AND $\text{C}_6\text{H}_5\text{O}^*$

CHIN-YU LIN

DEPARTMENT OF CHEMISTRY

THE CATHOLIC UNIVERSITY OF AMERICA

WASHINGTON D. C. 20064-0001

M. C. LIN⁺⁺

CHEMISTRY DIVISION

CODE 6105

NAVAL RESEARCH LABORATORY

WASHINGTON D. C. 20375-5000

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* work performed at NRL.

⁺⁺ Adjunct Professor of Chemistry, The Catholic University of America.

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INTRODUCTION

The reaction of CH_3 with $\text{C}_6\text{H}_5\text{O}$ has been shown by Mulcahy and Williams^{1,2} to produce o- and p-cresols via sigmatropic hydrogen transfer reactions involving methylcyclohexadienone intermediates:

Production of anisole (methylphenyl ether) by the combination reaction:

was, however, found to be a relatively minor process¹. These findings appear to be consistent with the expected resonance structures of the phenoxy radical²:

In our recent study of the unimolecular decomposition of the phenoxy radical in shock waves^{3,4},

we employed anisole as the radical source. The CO yields observed at long reaction times in the decomposition of highly diluted anisole-argon mixtures (0.1 - 0.7 %) were always found to be less than the starting anisole concentrations, $[An]_0$; i.e., $[CO]_{t=\infty}/[An]_0 < 1$. A typical set of CO production data is presented in Figure 1. The observed CO profiles could be satisfactorily modeled only if the reaction of CH_3 with C_6H_5O was included in the scheme⁴. The kinetic modeling of some 70 sets of data covering a wide range of temperature (1000 - 1580 K) and pressure (50 - 90 kPa) yielded to the rate constant, $(5.5 \pm 2.0) \times 10^{11} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, for the combination of CH_3 with C_6H_5O to form o- and p-cresols.

The objective of this work was to elucidate the mechanism of this reaction by correlating these high temperature data with those obtained from the modeling of the low temperature results measured some time ago by Mulcahy and Williams in their study of the $CH_3 + C_6H_5OH$ reaction carried out in a stirred flow reactor¹.

These two sets of data were analyzed on the basis of the RRKM theory^{5,6} by taking into account the formation and removal of the chemically activated methylcyclohexadienone intermediates (via collisional stabilization and isomerization into o- and p-cresols). The results of this analysis show that, at high temperatures, the reaction produces exclusively thermochemically stable cresols, while at low temperatures under the conditions used by Mulcahy and Williams, both stabilization and isomerization are equally important.

RESULTS AND DISCUSSION

Kinetic modeling of Mulcahy and Williams's data

The reaction between CH_3 and $\text{C}_6\text{H}_5\text{OH}$ was studied by Mulcahy and Williams¹ at total pressures ranging from 0.4 to 4.3 kPa and temperatures from 445 to 547 K in a stirred-flow reactor. The concentrations of $\text{C}_6\text{H}_5\text{OH}$ and CH_3 , generated by thermally decomposing di-*t*-butyl peroxide, were varied in the ranges $(0.1 - 8) \times 10^{-7}$ and $(0.2 - 4) \times 10^{-11} \text{ mol cm}^{-3}$, respectively. A list of 13 reactions was proposed by Mulcahy and Williams to account for the formation of methane and *o*- and *p*-cresols which were identified as major products in this system by GC analysis. However, the absolute rate constant for the reaction of interest, $\text{CH}_3 + \text{C}_6\text{H}_5\text{O}$, could not be determined by their kinetic analysis.

In an attempt to obtain the approximate value of the rate constant for the combination reaction in the low temperature region, we have computer-modeled the product distributions observed in Mulcahy and Williams' experiments¹ using their reaction mechanism, summarized as follows:

where X = methylcyclohexadienones, Yx = dimethylcyclohexadienones, Xy = dimethylphenols. Q is unidentified compound (or compounds) associated with "methyl loss"¹.

For kinetic modeling, the concentration of major products such as methane, ethane and cresols at certain residence times, t, should be known. The residence time in the stirred-flow experiment can be obtained⁷ by dividing the reaction vessel volume V by the volumetric rate of effluent gases, v. The concentration of each species c_i could be readily calculated from the rates of efflux of each species, n_i , and of all species, $\sum n_i$, measured in their study by the equation⁸:

$$c_i = n_i (\sum n_i)^{-1} [M] = n_i P (\sum n_i RT)^{-1} \quad (i),$$

where [M] is the total molecular concentration and P is the total pressure in the reactor. The rate constants used in this modeling are summarized in Table 1 and will be discussed below.

In Mulcahy and Williams' study, t-butoxy and methyl radicals were generated by the decomposition of di-t-butyl peroxide mixed with phenol vapor in a 276 ml stirred-flow reactor⁷. The production of CH_3 from t-butoxy radicals (reaction (2)) in the presence of phenol competes with reaction (3), $(\text{CH}_3)_3\text{CO} + \text{C}_6\text{H}_5\text{OH} \longrightarrow (\text{CH}_3)_3\text{COH} + \text{C}_6\text{H}_5\text{O}$. The rate constant for reaction (3), k_3 , can be evaluated by combining k_2 obtained from the literature¹⁰ and the relative rates determined by Mulcahy and Williams¹¹:

$$k_3/k_2 = n_{\text{tba}}(n_{\text{Ato}}[\text{PhOH}])^{-1} = w (1/\beta_B + 1/[\text{M}]) \quad (\text{ii}).$$

In eq.(II) n_{tba} and n_{Ato} are the rates of efflux of t-butanol (tba) and acetone (Ato), $[\text{PhOH}]$ is the concentration of phenol (PhOH), $w = n_{\text{tba}}(n_{\text{Ato}}[\text{PhOH}])^{-1}(1/\beta_B + 1/[\text{M}])^{-1}$ could be measured at different temperatures, and $\beta_B (=2.6 \times 10^6 \text{ mol cm}^{-3})$ is a constant regarded as independent of temperature.

The methyl radical recombination rate constant, k_7 , could be calculated according to the approximation equation,

$$k_4 = n_{\text{C}_2\text{H}_6} (V[\text{CH}_3]^2)^{-1} \quad (\text{iii}),$$

where V is the effective volume of the reactor (276 ml).

The rate constants for hydrogen abstraction by methyl radicals from methylocyclohexadienones (k_9) and dimethylocyclohexadienones (k_{12} assumed to be the same as k_9) were taken from Mulcahy and Williams' study¹ and the hydrogen abstraction from phenol (k_4) was increased by a factor of two to account for CH_4 formation in this system.

The rate constants for anisole and Q formation (k_5 and k_{13}) relative to cresol formation have been determined by Mulcahy and Williams¹. k_{10} (for Yx formation) and k_{11} (for the conversion of Yx to Xy by a hydrogen migration) can be reasonably assumed to be the same as k_6 and k_8 . Therefore, k_6 and k_8 are the only unknown parameters remaining in the modeling; they were adjusted to account for the formation of major products, methane and cresols, as well as the small amounts of anisole. In the modeling, k_6 was estimated from an RRKM calculation using the known rate constant obtained at 1250 K from the shock tube experiment⁴, as mentioned before, to extrapolate to the low temperature region, assuming no direct formation of cresols in the reaction. k_8 was evaluated by modeling the yields of cresols and the related derivatives. A least-squares analysis of the modeled values of k_8 gave rise to:

$$k_8 = 10^{15.7 \pm 2.3} \exp(-17,800 \pm 2,600/T) \text{ s}^{-1}.$$

The value of the frequency factor appears to be too high for this type of keto-enol conversion reactions, which are expected to involve rather tight activated complexes. This unreasonably high rate constant for reaction (8) is

most likely due to the exclusion of the direct cresol formation process, $\text{CH}_3 + \text{C}_6\text{H}_5\text{O} \longrightarrow \text{CH}_3\text{C}_6\text{H}_4\text{OH}$.

To estimate the relative importance of direct vs. indirect cresol formation, we employed a generalized mechanism which takes into account the formation and deactivation of the chemically activated methylocyclohexadienone intermediates, using the RRKM theory^{5,6}. Taking the formation of o-cresol as an example, this general mechanism can be given as follows:

The results of this calculation, as will be discussed in detail below, show that the direct formation of cresols via reaction (6') is at least as important as the formation of X via collisional deactivation, reaction (6).

In addition to reaction (6'), the following reactions are included in the scheme to account for the possible direct formation of Xy via reaction (10') and hydrogen abstraction by CH_3 from cresols by reaction (9'):

Here k_{10} , is assumed to be the same as k_6 , and k_9 , is about twice the value of k_4 used in the modeling (see Table 1).

Twenty sets of kinetic data obtained at different temperatures (445.3 K, 482.8 K, 516.1 K and 547.5 K) and total pressures (from 0.4 to 4.3 kPa) have been modeled with the generalized mechanism consisting of 16 reactions. Some of the modeled results are summarized in Table 2. The total rate ($k_6 + k_6'$) for $\text{CH}_3 + \text{C}_6\text{H}_5\text{O}$ was estimated from the RRKM calculation for each temperature. The formation of cresols was found to be sensitive to both the branching ratio (k_6/k_6') and k_8 , which are controlled by the barrier height of the transition state involved in the conversion of the thermalized X to cresols. The values of these rate constants were computed, with the aid of the RRKM theory, for different isomerization energy barriers via (6') and (8), assuming a tight activated complex. A value of 132 kJ mol^{-1} was found to fit most of the observed kinetic data. This value gave rise to

$$k_8 = 10^{13.3} \exp(-16,200/T) \text{ s}^{-1}$$

for the thermal isomerization of X to o- and p-cresols. Most of the calculated product yields, with the exception of Xy and Q (approximated to the "methyl loss") agree with the experimental values within a factor of two. It should be mentioned that the mechanism of Mulcahy and Williams also predicted very poor yields of Xy and Q which could not be fitted by increasing the values of k_{11} and k_{13} within reasonable limits. Both Xy and Q are subject to larger uncertainties.

The limits of k_6 , and the branching ratios shown in Figures 2 and 3, were obtained from the estimated total rates from the RRKM calculation, allowing for $\pm 5\%$ deviation from the exact fit of cresol concentrations. The branching ratios increase sharply as the temperature increases and or the total pressure decreases. The values of k_6/k_6 , varying from 0.8 to 6.4 under the conditions employed by Mulcahy and Williams, also indicate that at low temperatures the stabilization and isomerization processes are approximately equally important, and that the isomerization process becomes dominant at higher temperatures.

RRKM calculations

We have shown previously that the branching ratio for a multichannel bimolecular reaction occurring via a long-lived intermediate,

may vary very strongly with temperature and pressure^{5,6}. The RRKM rate constants for product formation via channels (c) and (d), are given respectively by the following equations^{5,6}:

$$k_{(c)} = \frac{1}{h} \frac{Q_t^{\ddagger} Q_r^{\ddagger}}{Q_A Q_{BC}} \exp(-E_{(a)}/RT) \int_0^{\infty} \frac{k_{E_1} \sum P(E_{(a)}^{\ddagger}) \exp(-E_{(a)}^{\ddagger}/RT) dE_{(a)}^{\ddagger}}{\sum_i k_{E_i} + w} \quad (iv)$$

$$k_{(d)} = l_{(a)} \frac{kT Q_t^\ddagger Q_r^\ddagger}{h Q_A Q_{BC}} \exp(-E_{(a)}/RT) \int_0^\infty \frac{w \sum P(E_{(a)}^\ddagger) \exp(-E_{(a)}^\ddagger/RT) dE_{(a)}^\ddagger}{\sum_i k_{E_i} + w} \quad (v)$$

where $i = (b), (c), (d)$ and $l_{(a)}$ is the reaction path degeneracy for the formation of the chemically activated adduct, $ABC^\ddagger$, via step (a). Q_A and Q_{BC} are the total (translational, rotational and vibrational) partition functions of A and BC, respectively. $Q_t^\ddagger$ and $Q_r^\ddagger$ are the translational and rotational partition functions of the transition state $ABC^\ddagger$ associated with step (a), which has a reaction barrier of $E_{(a)}$ at 0 K. In the present case, $E_{(a)}$ is assumed to be zero. The quantities under the integral sign: $\sum P(E_i^\ddagger)$ is the sum of the states of the activated complex of the i th channel possessing excess energy $E_i^\ddagger$; w is the effective collision frequency for the deactivation of the excited adduct, which can be evaluated by the method of Troe¹²; k_{E_i} is the specific rate constant for the decomposition (or isomerization as in the present case) of the excited adduct via the i th channel. According to the RRKM theory¹³,

$$k_{E_i} = l_i (I_i^\ddagger/I)^{1/2} \sum P(E_i^\ddagger) (hN(E))^{-1} \quad (vi)$$

Here l_i is again the reaction path degeneracy for step (i); $I_i^\ddagger/I$ is the ratio of the product of the three overall moments of inertia of the activated complex (i) to that of the adduct ABC; $N(E)$ is the density of the states of ABC at the total energy E .

To evaluate $k_{(c)}$ and $k_{(d)}$, the energies and structures of all species (reactants, the activated complexes and the excited adduct) must be estimated. The heats of formation of all species related to the present system, including the adduct, are listed in Table 3. The heats of formation of the adduct, $\Delta H_f^0(\text{CH}_3\text{C}_6\text{H}_5\text{O}) = -69 \text{ kJ mol}^{-1}$, was estimated by using the relevant C-H bond strengths¹⁷, $D(\text{R}'-\text{R})$, in cycloalkadienes and the well-known bond energy difference¹⁷, $D(\text{R}_3\text{C}-\text{H}) - D(\text{R}_3\text{C}-\text{CH}_3) = 41.8 \pm 8.4 \text{ kJ mol}^{-1}$, as follows:

R'-R

D(R'-R)	297.2 ± 8.4	305.4 ± 20.9	305.4 ± 8.4	305.4	263.6
(kJ mol ⁻¹)				(assumed)	

The energy diagram of the system is shown in Figure 4.

The vibrational frequencies of the adduct were estimated on the basis of the spectra of p-benzoquinone¹⁸ and toluene¹⁹. The transition state for channel (a) or (b) was assumed to be loose, with two CH₃ rocking frequencies decreased and the torsional vibration converted to free internal rotation to account for the observed recombination rate constant at high temperatures⁴. The transition state (c) involves the transfer of the tertiary H atom; it is assumed to be tight, and thus all molecular parameters are taken to be the

same as those of the adduct, except one of the C-H bending vibrations associated with the recombination site becomes the reaction coordinate and another bending frequency is decreased. All vibrational frequencies are summarized in Table 4 together with the values of moments of inertia and the collisional step-sizes for argon and C_6H_5OH deactivators.

The branching ratios ($k_{(c)}/k_{(d)}$ or k_6/k_6) of isomerization to stabilization at low temperatures (445 - 547 K) were found to depend strongly on the energy barrier assumed for step (c), in addition to the temperature and pressure of the system. As mentioned before, we found that a barrier of 132 kJ mol^{-1} above the ground state adduct led to the most reasonable fits for observed key product yields. This barrier height also appears to be reasonable for H-migration involved in a four-centered complex. The predicted and observed branching ratios based on this barrier height are shown in Figure 3 for different temperatures and total pressures.

The computed $k_{(c)}$ (or k_6 , for the formation of cresols) as a function of temperature and pressure is presented in Figure 2 using argon and C_6H_5OH as collision partners. Also shown in this figure is $k_{(d)}$ (or k_6 for the stabilization channel), which is important only at low temperatures.

CONCLUSION

A mechanism consisting of 16 reactions was used to model the product distributions of the reaction of CH_3 and C_6H_5OH measured by Mulcahy and Williams. The key paths for cresol formation are believed to involve

vibrationally excited methylcyclohexadienone intermediates. The general mechanism for $\text{CH}_3 + \text{C}_6\text{H}_5\text{O}$ leading to o-cresol, for instance, can be depicted as follows:

The branching ratio k_6'/k_6 and the thermal rate k_8 have been deduced from kinetic modeling and RRKM calculations. An energy barrier of about 132 kJ mol^{-1} has been estimated for the H-migration process.

This reaction scheme can satisfactorily correlate the modeled low temperature results and high temperature kinetic data recently obtained from our shock tube study. At low temperatures, both isomerization and stabilization are important in the combination reaction, whereas at high temperatures ($T > 1200 \text{ K}$), isomerization to cresols is the major pathway.

ACKNOWLEDGMENT

C.-Y. Lin gratefully acknowledges the financial support of The U. S. Department of Energy, Division of Chemical Sciences, under Contract No. DE-FG05-85ER13373.

REFERENCES

- ¹ Mulcahy, M. F. R., and Williams, D. J., Aust. J. Chem., 1965, 18, 20.
- ² Mulcahy, M. F. R., and Williams, D. J., Nature, 1963, 199, 761.
- ³ Lin, C.-Y., and Lin, M. C., Int. J. Chem. Kinet., 1985, 17, 1025.
- ⁴ Lin, C.-Y., and Lin, M. C., J. Phys. Chem., in press.
- ⁵ Berman, M. R., and Lin, M. C., J. Phys. Chem., 1983, 87, 3933.
- ⁶ Hsu, D. S. Y., Shaub, W. M., Creamer, T., Gutman, D., and Lin, M. C., Ber. Bunsenges. Phys. Chem., 1983, 87, 909.
- ⁷ Mulcahy, M. F. R., and Williams, D. J., Aust. J. Chem., 1961, 14, 534.
- ⁸ Mulcahy, M. F. R., and Williams, D. J., and Wilmshurst, J. R., Aust. J. Chem., 1964, 17, 1329.
- ⁹ Shaw, D. H., and Pritchard, H. O., Can. J. Chem., 1968, 46, 2721.
- ¹⁰ Batt, L., and Cruickshank, F. R., J. Phys. Chem., 1967, 71, 1836.
- ¹¹ Mulcahy, M. F. R., and Williams, D. J., Aust. J. Chem., 1964, 17, 1291.
- ¹² Troe, J., J. Chem. Phys., 1977, 66, 4745.
- ¹³ Robinson, P. J., and Holbrook, K. A., "Unimolecular Reactions", Wiley, New York, 1972.
- ¹⁴ Baghal-Vayjooee, M. H., Colussi, A. J., and Benson, S. W., Int. J. Chem. Kinet., 1979, 11, 147.
- ¹⁵ Colussi, A. J., Zabel, F., and Benson, S. W., Int. J. Chem. Kinet., 1977, 9, 161.
- ¹⁶ Halverson, F., and Francel, R. J., J. Chem. Phys., 1949, 17, 694.
- ¹⁷ McMillen, D. F., and Golden, D. M., Ann. Rev. Phys. Chem., 1982, 33, 493.
- ¹⁸ Dunn, T. M., and Francis, A. H., J. Mol. Spectrosc., 1974, 50, 1.
- ¹⁹ Fuson, N., Garnigou-Lagrange, C., and Josien, M. L., Spectrochim Acta, 1960, 16, 106.

TABLES

Table 1. Rate constants used in the kinetic modeling of the $[(CH_3)_3CO]_2$
+ C_6H_5OH system^a.

Reaction	k^b	Source
(1)	$6.3 \times 10^{15} \exp(-19,000/T)$	Ref. 9
(2)	$3.2 \times 10^{13} \exp(-8,250/T)$	Ref. 10
(3)	$(0.1 - 3.8) \times 10^{12}$	Ref. 11, temperature dependent
(4)	$(0.6 - 2.6) \times 10^8$	Ref. 1, temperature dependent
(5)	$0.07 (k_6 + k_{6'})$	Ref. 2
(6)	$(0.4 - 1.6) \times 10^{11}$	Kinetic modeling with the aid of RRKM calculations
(6')	$(1.3 - 2.8) \times 10^{11}$	Kinetic modeling with the aid of RRKM calculations
(7)	$(1.0 - 3.0) \times 10^{13}$	Ref. 8, pressure dependent
(8)	$2.0 \times 10^{13} \exp(-16,200/T)$	Kinetic modeling with the aid of RRKM calculations ^c
(9)	$(0.2 - 1.4) \times 10^{10}$	Ref. 1, temperature dependent
(9')	$(1.2 - 5.2) \times 10^8$	Ref. 1, temperature dependent
(10)	same as k_6	assumed
(10')	same as $k_{6'}$	assumed
(11)	same as k_8	assumed
(12)	same as k_9	assumed
(13)	$7.3(k_6 + k_{6'})$	Ref. 1

a. These are finalized rate constants used in the modified mechanism, including reactions (6'), (9') and (10').

b. k is in cm^3 , mol and s units.

c. Total rate constants for o- and p- cresol formation from X.

Table 2. Experimental and calculated product yields in the $[(\text{CH}_3)_3\text{CO}]_2 + \text{C}_6\text{H}_5\text{OH}$ system^a.

Expt. No.	78	42	48	43	111	110	122	9	7	76
T(K)	445.3	482.4	482.3	481.8	482.7	481.9	516.1	516.6	516.1	547.1
P(kPa)	3.4	3.8	3.4	3.3	2.1	1.6	1.5	1.3	1.3	0.5
t(s) ^b	110.	11.7	11.8	12.7	15.9	18.6	1.4	1.43	1.47	0.57
$10^8[\text{dbp}]$ Exptl.	33.8	22.7	11.2	8.63	-	1.7	2.68	1.83	2.01	0.1
Calc.	34.8	23.2	12.2	9.31	1.54	1.54	2.85	1.72	1.78	0.02
$10^8[\text{Ato}]$ Exptl.	14.7	37.1	15.6	12.5	2.93	3.34	7.44	4.02	4.19	0.45
Calc.	13.1	32.9	15.8	12.4	3.36	3.47	7.43	4.85	4.96	0.63
$10^{12}[\text{CH}_3]$ Exptl.	3.78	25.4	14.7	12.3	6.38	5.24	36.4	27.1	27.5	19.5
Calc.	3.77	22.0	14.0	10.5	5.32	4.27	28.0	23.5	22.2	8.48
$10^7[\text{PhOH}]$ Exptl.	2.85	1.43	4.56	5.10	1.24	3.31	2.03	2.27	2.04	0.94
Calc.	3.16	1.40	4.54	5.08	1.22	3.29	2.02	2.24	2.02	0.95
$10^9[\text{tba}]$ Exptl.	27.9	12.8	24.4	20.8	1.73	6.13	4.66	3.11	2.72	0.20
Calc.	18.6	13.3	21.6	19.2	1.84	5.95	4.18	3.29	3.40	0.28
$10^8[\text{C}_2\text{H}_6]$ Exptl.	3.15	15.1	4.94	3.74	1.19	0.91	3.04	1.71	1.77	0.21
Calc.	4.42	15.0	5.65	4.16	1.44	1.05	3.23	2.01	2.08	0.28
$10^9[\text{CH}_4]$ Exptl.	18.9	15.1	17.8	15.2	1.35	4.02	2.56	1.75	1.75	0.20
Calc.	11.9	7.65	12.0	11.2	1.50	4.01	2.95	2.67	2.52	0.29
$10^{10}[\text{An}]$ Exptl.	25.5	8.52	21.4	18.5	2.88	6.34	5.57	2.23	2.14	0.39
Calc.	18.9	11.5	19.5	17.9	2.06	5.97	4.40	3.57	3.55	0.28
$10^9[\text{Cre}]$ Exptl.	21.6	9.67	18.4	17.5	2.47	5.80	5.72	3.38	3.20	0.39
Calc.	21.5	9.56	18.1	17.5	2.47	5.87	5.69	3.35	3.23	0.39
$10^9[\text{Q}]$ Exptl.	18.7	(20.0)	7.72	6.46	0.55	2.09	2.02	0.03	(0.91)(-0.16)	
Calc.	1.86	2.78	2.85	2.19	0.11	0.50	0.11	0.17	0.19	0.003
$10^{10}[\text{Xy}]$ Exptl.	12.3	11.5	14.2	14.8	1.15	2.36	2.02	2.44	-	0.20
Calc.	2.17	2.31	2.60	2.10	0.12	0.52	0.14	0.16	0.17	0.004

Table 2. (Cont'd)

a. The experimental data are from Ref. 1.

b. t : residence time, $t = V.v^{-1}$ ($V = 276$ ml)

dbp: di-*t*-butyl peroxide

Ato: acetone

PhOH: phenol

tba: *t*-butanol

An: anisole

Cre: cresols

Q: unidentified compound(s) related to "methyl loss"

Xy: dimethylphenols

The concentrations are in mol cm^{-3} .

The figures given in parentheses are subject to especially large errors and

"-" represents that the value is not measurable.

Table 3. Thermochemical data for species involved in the $\text{CH}_3 + \text{C}_6\text{H}_5\text{O}$ reaction

species	ΔH_f^0 , 298 K (kJ mol ⁻¹)	Source
CH_3	146.9	Ref. 14
$\text{C}_6\text{H}_5\text{O}$	47.7	Ref. 15
$\text{CH}_3\text{C}_6\text{H}_5\text{O}$	-69.0	Estimated, see text.
$\text{o-CH}_3\text{C}_6\text{H}_4\text{OH}$	-125.9	Ref. 16

Table 4. Parameters used in the RRKM calculations of the $\text{CH}_3 + \text{C}_6\text{H}_5\text{O}$ reaction (i)

parameter	ground state	transition states	
		(a)	(c)
ν (cm^{-1})	3018 (8)	3018 (8)	3018 (8)
	1408 (10)	1408 (10)	1408 (10)
	1139 (8)	1168 (5)	1135 (7)
	871 (6)	871 (6)	849 (6)
	610 (6)	610 (6)	610 (6)
	402 (3)	402 (3)	402 (3)
	289 (1)	71 (2)	289 (1)
$10^{40} I_r$ (g cm^2)		2.9 (1)	
$(I^\ddagger/I)^{1/2}$		2.1	1.0
$\langle \Delta E \rangle_{\text{argon}}$ (kJ mol^{-1})	4.2 (ii)		
$\langle \Delta E \rangle_{\text{PhOH}}$ (kJ mol^{-1})	41.8 (ii)		

(i) The structures of the ground state and transition states (a) and (c) are assumed as follows:

(ii) Average amounts of energy transferred per collision.

FIGURE CAPTIONS

Fig. 1. Observed and modeled CO production profiles at 1345 K for 0.264 % anisole-argon mixture at $P = 59.2$ kPa; circles: experimental results, solid and dashed lines: modeled results with and without inclusion of the $\text{CH}_3 + \text{C}_6\text{H}_5\text{O}$ reaction (Data from Ref. 4).

Fig. 2 Temperature and pressure effects on k_6 and $k_{6'}$.
 Filled circles: shock tube results for 66.7 kPa argon, $T = 1000 - 1580 \text{ K}^4$.
 Open symbols: evaluated rate constants based upon the modeled $k_{6'}/k_6$ ratios by fitting Mulcahy and Williams' data and the total rate ($k_6 + k_{6'}$) from RRKM calculations.
 Δ : 0.7 ± 0.2 kPa, $\bigcirc$: 1.2 ± 0.2 kPa, $\square$: 1.9 ± 0.2 kPa,
 ∇ : 2.9 ± 0.7 kPa, $\diamond$: 4.1 ± 0.4 kPa.
 Solid and dashed curves: calculated results for $k_{6'}$ and k_6 respectively at different pressures of deactivator as indicated.

Fig. 3. The branching ratio for isomerization to stabilization as a function of temperature and pressure using phenol as a third body; symbols are the same as those in Fig. 2 (The error bars shown are with $\pm 5\%$ deviation from the exact fit for cresols formation). Solid and dashed curves are the results of RRKM calculations.

Fig. 4 Energy diagram for the combination reaction of CH_3 with $\text{C}_6\text{H}_5\text{O}$ producing $\text{o-CH}_3\text{C}_6\text{H}_4\text{OH}$.

Fig. 1

Fig. 2

Fig. 3

Fig. 4

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