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Kinetics of Radiation-Induced Hydrogen Abstraction by CCl_3 Radicals in the Liquid Phase. Secondary Alcohols

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The dependence of the yields of products in the γ-radiation-induced free-radical reactions in carbon tetrachloride solutions of secondary alcohols on the alcohol concentration and temperature was studied in the range of 0.05–0.6 M and 30–150 °C. The rate constant for the reaction $CCl_3 + R_1R_2CHOH \rightarrow CHCl_3 + R_1R_2COH$ (k_1) was found as $\log k_1$ ($M^{-1}\ s^{-1}$) $= 8.63 - 9.1/\theta$, where $\theta = 2.303RT$ kcal mol^{-1}. The activation energy is 1.8 ± 0.3 kcal mol^{-1} lower than for secondary hydrogens in alkanes and about the same as for the tertiary hydrogens in 2,3-dimethylbutane.

Introduction

Hannerz[1] studied the radiolysis of a 50 vol % mixture of carbon tetrachloride with primary and secondary alcohols and obtained very large G values for HCl (number of molecules produced per 100 eV of energy absorbed) indicating a chain reaction. Radlowski and Sherman[2] studied the γ radiolysis of deaereated 2-propanol solutions of carbon tetrachloride and proved that the mechanism is

initiation

$$\text{2-propanol} \rightarrow \text{radicals (Xi)}$$

$$Xi + CCl_4 \rightarrow XiCl + CCl_3$$

propagation

$$\dot{C}Cl_3 + (CH_3)_2CHOH \rightarrow CHCl_3 + (CH_3)_2\dot{C}OH \quad (1)$$

$$(CH_3)_2\dot{C}OH + CCl_4 \rightarrow (CH_3)_2C{=}O + HCl + \dot{C}Cl_3 \quad (2)$$

termination

$$2\dot{C}Cl_3 \rightarrow C_2Cl_6 \quad (3)$$

They showed that the chain reaction does not involve carbon tetrachloride in the rate-determining step whereas the rate-determining step involves one molecule of 2-propanol. Thus reaction 1 is the rate-determining step and hence

$$G(CHCl_3) = G(\text{acetone}) = \frac{k_1}{k_3^{1/2}}[\text{2-propanol}](G(Xi)\alpha)^{1/2}$$

where α is the factor transforming from rate of formation to G values and equals $(100N/I)$ where N is Avogadro's number and I is the dose (eV/(L s)). Radlowski and Sherman assumed G(Xi) to be equal to the yield of radicals in 2-propanol as measured by Adams et al.[3] Assuming $k_3 = 1 \times 10^8\ M^{-1}\ s^{-1}$, they obtained at room temperature $k_1 = 2.9\ M^{-1}\ s^{-1}$. A better way which will not need the assumption of reaction 3 as the only termination reaction[4] is the measurement of the yield of C_2Cl_6 which can be written[5]

$$\frac{G(CHCl_3)}{G^{1/2}(C_2Cl_6)} = \frac{k_1}{k_3^{1/2}}[RH]\alpha^{1/2}$$

where RH is the molecule from which hydrogen is abstracted.

No studies were done on this system at other than room temperature and hence the activation energy E_3 could be found only by assigning an A factor.[6]

This work was undertaken in order to determine the Arrhenius parameters for the abstraction of hydrogen atoms from two secondary alcohols: 2-propanol and cyclohexanol. In order to be able to compare the results of the two compounds and to compare them to alkanes we used CCl_4 as the solvent,[5,7] and not the alcohol itself as was done in the study of Radlowsky and Sherman, to eliminate the problem of different activation energies for diffusion.

Method

The mechanism for the radiolysis of carbon tetrachloride solutions of secondary alcohols is

initiation

$$CCl_4 \xrightarrow{\gamma} \dot{C}Cl_3 + Cl$$

$$Cl + R_1R_2CHOH \rightarrow HCl + R_1R_2\dot{C}OH$$

$$R_1R_2\dot{C}OH + CCl_4 \rightarrow R_1R_2CO + HCl + \dot{C}Cl_3$$

Thus the initiation step can be summed up as

$$2CCl_4 + R_1R_2CHOH \rightarrow 2HCl + R_1R_2CO + 2\dot{C}Cl_3$$

propagation

$$CCl_3 + R_1R_2CHOH \xrightarrow{\text{slow}} CHCl_3 + R_1R_2\dot{C}OH \quad (1)$$

$$R_1R_2\dot{C}OH + CCl_4 \xrightarrow{\text{fast}} R_1R_2CO + HCl + CCl_3 \quad (2)$$

termination

$$CCl_3 + CCl_3 \rightarrow C_2Cl_6 \quad (3)$$

Other ways of termination, as the reactions of $\dot{C}Cl_3$ with $R_1R_2\dot{C}OH$ or two $R_1R_2\dot{C}OH$ radicals, are also possible. However, except in the case of cholesteryl esters,[8] it was found that for CCl_4 solutions reaction 3 is the sole termination reaction.[5,8]

For the propagation steps

$$G(CHCl_3) = G(HCl) = G(\text{ketone})$$

However, HCl and ketone are formed also in the initiation step, although with different yields, while chloroform is not produced in this step. The yield from the initiation step can be deduced from the yield of C_2Cl_6, since the yield

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[1] K. Hannerz, *Research*, 9, 51 (1956).

[2] C. Radlowski and W. V. Sherman, *J. Phys. Chem.*, 74, 3043 (1970).

[3] G. E. Adams, J. H. Baxendale, and R. D. Sedgwick, *J. Phys. Chem.*, 63, 854 (1959).

[4] Z. B. Alfassi, *Int. J. Chem. Kinet.*, 12, 217 (1980).

[5] Z. B. Alfassi and L. Feldman, *Int. J. Chem. Kinet.*, 12, 379 (1980).

[6] D. G. Hendry, T. Mill, L. Piszkiewicz, J. A. Howard, and H. K. Eigenmann, *J. Phys. Chem. Ref. Data*, 3, 937 (1974).

[7] M. G. Katz, G. Baruch, and L. A. Rajbenbach, *Int. J. Chem. Kinet.*, 10, 905 (1978).

[8] L. Feldman and Z. B. Alfassi, *Radiat. Phys. Chem.*, 15, 687 (1980).

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TABLE I: Radiolytic Yields in the Radiolysis of Carbon Tetrachloride Solutions of Secondary Alcohols

2-propanol				cyclohexanol			
T, °C	[RH], M	G(acetone)	$G(C_2Cl_6)$	T, °C	[RH], M	$G(CHCl_3)$	$G(C_2Cl_6)$
33	0.10	6.13	3.83	30	0.05	1.74	3.81
	0.20	8.00	4.39		0.10	3.07	3.95
	0.40	11.7	4.13		0.20	6.58	4.25
	0.60	15.4	4.61		0.40	10.6	4.14
66	0.05	7.11	4.51	50	0.05	2.75	3.78
	0.10	9.68	4.26		0.10	5.82	4.07
	0.20	15.0	4.12		0.40	21.9	3.73
	0.40	28.3	4.19	62	0.10	7.81	4.37
74	0.10	10.2	4.54		0.20	16.3	4.22
	0.20	18.7	4.83		0.40	29.7	4.22
	0.40	39.8	4.98		0.60	46.4	4.19
	0.60	61.2	5.43	73	0.05	6.24	4.16
90	0.10	11.0	4.04		0.10	9.76	3.84
	0.20	30.9	4.04		0.20	24.0	4.11
	0.60	84.8	4.04		0.40	37.8	3.73
104	0.05	11.0	4.25	75	0.05	4.54	4.00
	0.10	22.3	4.40		0.10	11.0	3.68
	0.20	38.3	4.28		0.20	17.1	3.88
	0.40	77.5	5.10		0.40	42.5	3.73
112	0.20	53.0	4.54	90	0.05	11.7	4.11
	0.40	114	4.67		0.10	20.8	4.11
	0.60	160	4.43		0.20	37.1	3.99
127	0.05	18.9	4.45		0.40	65.6	4.21
	0.10	36.8	4.83	112	0.05	18.3	4.18
	0.20	69.4	4.22		0.10	32.4	3.96
	0.40	138	4.83		0.20	72.4	3.91
144	0.05	29.8	4.25		0.40	148	3.84
	0.10	57.6	4.68	144	0.05	36.3	4.22
	0.20	103	4.36		0.10	64.5	4.11
	0.40	217	4.42		0.20	158	4.38
					0.40	258	4.08
				155	0.05	58.0	4.45
					0.10	111	4.18
					0.20	255	4.11

TABLE II: $k_1/k_3^{1/2}$ Values ($M^{-1}\ s^{-1/2}$) for Cyclohexanol and 2-Propanol, Calculated from Least Squares According to Eq C

2-propanol		cyclohexanol		
T, °C	$(k_1/k_3^{1/2})\cdot 10^3$	T, °C	$(k_1/k_3^{1/2})\cdot 10^3$	corrected $(k_1/k_3^{1/2})\cdot 10^3$
33	3.75 ± 0.37	30	5.97 ± 0.66	5.25
66	12.4 ± 0.7	50	12.4 ± 0.2	10.6
74	16.6 ± 0.9	62	16.2 ± 0.2	13.2
90	28.8 ± 1.3	73	22.3 ± 1.0	17.6
104	34.6 ± 0.1	75	23.1 ± 0.9	18.0
112	53.3 ± 1.0	90	36.3 ± 1.8	27.6
127	65.7 ± 0.6	112	81.1 ± 1.6	62.9
144	107 ± 1	144	143 ± 2	97.7
		155	263 ± 6	203

of the initiation step has to be equal to the yield of the termination, thus

$$G(\text{ketone}) = G(CHCl_3) + G(C_2Cl_6) \qquad (A)$$

$$G(HCl) = G(CHCl_3) + 2G(C_2Cl_6) \qquad (B)$$

Reaction 1 leads to the following rate equation:

$$d[CHCl_3]/dt = k_1[CCl_3][RH]$$

the steady-state concentration of the CCl_3 radicals can be deduced from the yield of C_2Cl_6 (reaction 3)

$$[C_2Cl_6] = k_3[CCl_3]^2t$$

Combining these two equations gives

$$\frac{G(CHCl_3)}{G^{1/2}(C_2Cl_6)} = \frac{k_1}{k_3^{1/2}}(RH)\alpha^{1/2} \qquad (C)$$

where (RH) is the concentration of the secondary alcohols.

Experimental Results

Samples of 1 mL of CCl_4 solutions of 2-propanol and cyclohexanol were prepared by degassing under liquid nitrogen (three cycles of thawing and freezing). For solutions of cyclohexanol, the yields of $CHCl_3$ and C_2Cl_6 were measured gas chromatographically with a flame ionization detector using a column of 10% SF-96. With 2-propanol as a solute it was not possible to measure $CHCl_3$ due to overlapping and thus we measure the yield of acetone, and the yield of $CHCl_3$ was calculated from eq A. Acetone was separated on a column of 10% diethylhexylphosphoric acid.

A ^{60}Co gammacell with a dose rate of 0.365 Mrd/h was used. Dosimetry was performed with a Fricke dosimeter and by calculating the dose for CCl_4 solution in accordance with the electron density. The temperature during irradiation was maintained within ±1 °C by an electric glycerine thermostat.

The radiolytic yields of $CHCl_3$, C_2Cl_6, and acetone are given in Table I. Table II gives $k_1/k_3^{1/2}$ for the two alcohols calculated for cyclohexanol from least squares according to eq C and for 2-propanol from eq A and C together. The errors given are one standard deviation. Examples of the fit of the experimental results to eq C are given in Figures 1 and 2. These results indicate that the rate-determining step is first order for the secondary alcohols. The $G(C_2Cl_6)$ values used for eq C are not those presented in Table I, but those in Table I after subtraction of 0.45 which was found to be the "molecular" yield of CCl_4.[8,23] This molecular yield comes from nonradical processes and hence does not take part in our system. In any case, this "molecular" contribution is small compared to most of our results and actually can be neglected.

The independence of the C_2Cl_6 yield within experimental error of the concentration of the secondary alcohol (Table

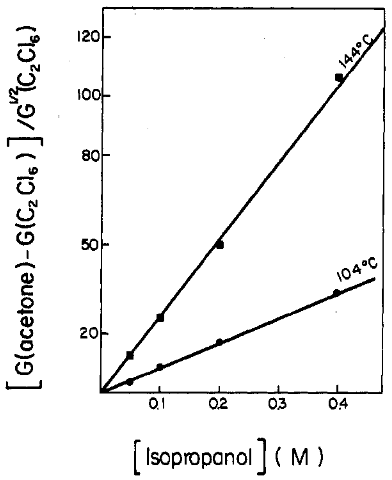

Figure 1. Dependence of $[G(\text{acetone}) - G(C_2Cl_6)]/G^{1/2}(C_2Cl_6)$ on the concentration of 2-propanol in carbon tetrachloride solutions at 104 (●) and 144 °C (■).

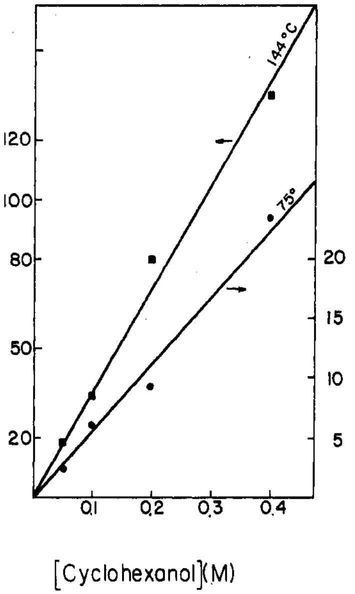

Figure 2. Dependence of $G(CH_3Cl)/G^{1/2}(C_2Cl_6)$ on the concentration of cyclohexanol in carbon tetrachloride solutions at 75 (●) and 144 °C (■).

I) shows that the assumption of termination by only $CCl_3 + CCl_3$ was justified. The constancy of the yield of C_2Cl_6 indicates that the concentration of CCl_3 is independent of the concentration of R_1R_2CHOH. The sum of the concentrations $[CCl_3] + [R_1R_2COH]$ is constant and equals the rate of formation of radicals by γ radiation. The ratio of the concentration of the radicals depends on the concentration of the alcohols; assuming long chains leads to

$$\frac{[CCl_3]}{[R_1R_2COH]} = \frac{k_2[CCl_4]}{k_1[R_1R_2CHOH]}$$

The constancy of $[CCl_3]$ together with the change in the ratio means that most of the radicals are CCl_3, due to $k_2 >> k_1$, which lead to termination by $CCl_3 + CCl_3$.

The Arrhenius parameters for $k_3/k_1^{1/2}$ are given in Table III and the Arrhenius plots in Figures 3 and 4. For 2-propanol, since we measured acetone, this means we measured the abstraction of hydrogen from the α carbon only. In the case of abstraction by iodine atoms[9] and CH_3 radicals[10] it was found that this is the main source of hydrogen atoms. However, in the case of cyclohexanol, hy-

TABLE III: Arrhenius Parameters for Abstraction of Hydrogen Atoms

	$E_1 - {}^1/_2E_3$, kcal mol^{-1}	$\log A_1 - {}^1/_2 \log A_3$, $M^{-1/2}\ s^{-1/2}$
2-propanol	7.63 ± 0.21	2.99 ± 0.13
cyclohexanol	7.65 ± 0.34	3.19 ± 0.21
corrected cyclohexanol	7.26 ± 0.43	2.85 ± 0.26
average of 2-propanol and corrected cyclohexanol	7.45	2.92

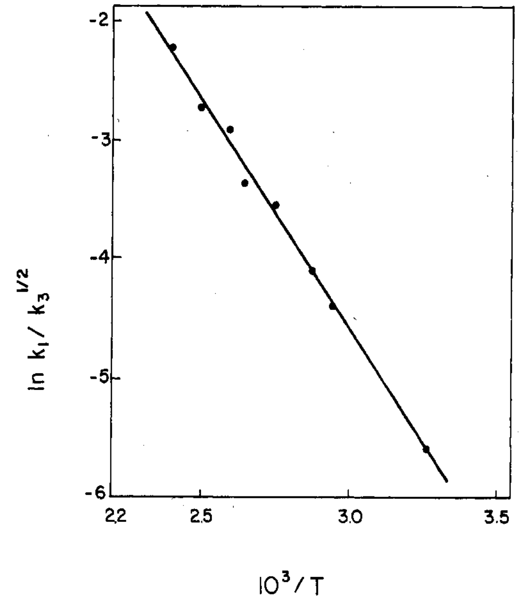

Figure 3. The Arrhenius plot for $k_1/k_3^{1/2}$ in the case of 2-propanol.

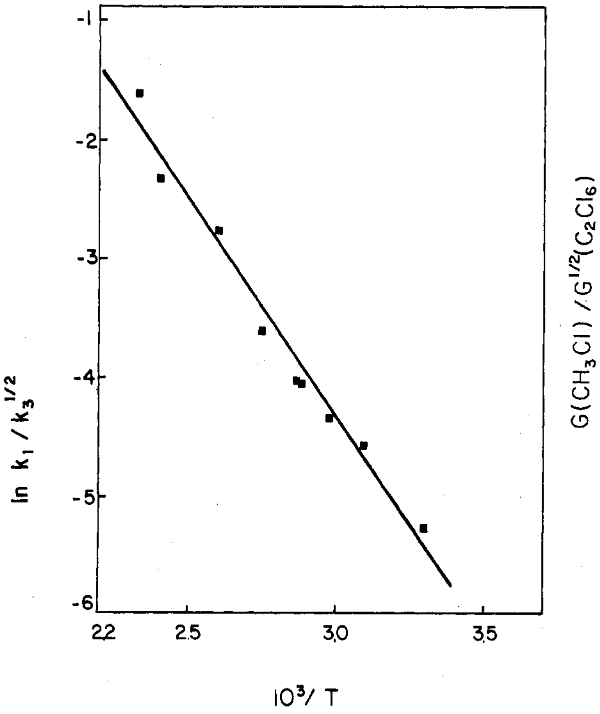

Figure 4. The Arrhenius plot for the corrected $k_1/k_3^{1/2}$ in the case of cyclohexanol.

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[9] R. Walsh and S. W. Benson, *J. Am. Chem. Soc.*, 88, 3480 (1966).

[10] P. Gray, A. A. Herod, and A. Jones, *Chem. Rev.*, 71, 247 (1971).

drogen atoms can be abstracted both from the α carbon and other carbon atoms. To obtain the rate constant for the abstrction of α hydrogen only, the rate constant for the abstraction of non α hydrogens has to be subtracted from our experimental results. The rate constant for the abstraction of non α hydrogen can be found by assuming that the hydroxyl group has no effect on the rate of abstraction from the other carbon atoms except the α carbon. The data for the rate of abstraction of hydrogen from cyclohexane[11] ($k_1/k_3^{1/2} = \exp[8.12 - 4.6/T]$) can be used to calculate the rate of the abstraction from the non α carbon atoms (multiplying by 5/6). Figure 4 gives the Arrhenius plot of the "corrected" $k_1/k_3^{1/2}$ for cyclohexanol and the results are given in Table III.

Discussion

The rate constant for abstraction of hydrogen from 2-propanol by CCl_3 radicals was measured at room temperature by three groups. None of them measured C_2Cl_6 but rather assumed C_2Cl_6 to be the only termination product and assigned $G(C_2Cl_6) = {}^1/_2G(\text{radicals})$. Van Beek and van der Stoep[12] studied the acetone-sensitized photochemical dehalogenation of CCl_4 in 2-propanol and obtained $k_1/k_3^{1/2} = 3.34 \times 10^{-3}\ M^{-1/2}\ s^{-1/2}$ as compared to Radlowsky and Sherman result in the γ radiolysis of a 2-propanol solution of CCl_4 of $k_1/k_3^{1/2} = 2.9 \times 10^{-4}\ M^{-1/2}\ s^{-1/2}$. Koster and Asmus measured the reaction of CCl_3 with 2-propanol in aqueous solution and obtained $k_1/k_3^{1/2} = 2.5 \times 10^{-3}\ M^{-1/2}\ s^{-1/2}$. Our result at 33 °C ((3.7 ± 0.4) × 10^{-3}) is close to the first and last results. No previous measurement of the activation energy was done except for the calculation of the activation energy from the Radlowsky and Sherman rate constant by assigning an A factor.[6]

Arrhenius Parameters. To calculate the Arrhenius parameters for hydrogen abstraction, k_1, we must know the Arrhenius parameters for the combination reaction of two CCl_3 radicals. For reasons discussed in previous papers,[5,8,14] it seems more correct to assume that this reaction is not temperature independent but rather diffusion controlled, with an activation energy equal to that of the self-diffusion of CCl_4 (3.3 kcal/mol)[15] and an A factor which was found for the same reaction in methanol[16] (log A ($M^{-1}\ s^{-1}$) = 11.42). The Arrhenius parameters found for R_1R_2CHOH (Table III) are the same within experimental error for both 2-propanol and cyclohexanol and using the value of k_3 leads to the expression

$$\log k_1\ (M^{-1}\ s^{-1}) = 8.13 - 9.1/\theta$$

where θ is $2.303RT$ in kcal mol^{-1}.

Activation Energies. Comparison with Alkanes. In the abstraction of hydrogen atoms by CCl_3 radicals from alkanes, it was found that the activation energy for abstraction from a CH_2 group is 10.7 kcal mol^{-1} [11,14,17] whereas for the abstraction from a CH group (in 2,3-dimethylbutane[5]), it is only 8.7 kcal mol^{-1}. Our results show that the abstraction from a CH group in secondary alcohols has activation energy of 9.1 ± 0.4 kcal mol^{-1}. Thus the effect of an OH group in a secondary alcohol on the activation energy is almost the same as of a methyl group. This fact agrees with the values of the bond dissociation energies; however, for the bond dissociation energy an OH group has a slightly larger effect than a methyl group[9,18] whereas for activation energies the opposite is true.

Comparison of CH_3 and CC_3 Radicals. Herod[19] studied the abstraction of an H atom from 2-propanol by a CH_3 radical and obtained an activation energy of 7.9 kcal/mol, 1.2 kcal/mol less than for CCl_3. A similar situation of lower activation energy for a CH_3 radical exists for abstraction from a CH_2 group, except that from a CH_2 group the activation energy for abstraction by a CCl_3 radical is higher by only 0.7 kcal mol^{-1}.[17]

A Factors. Our log A factor of 8.6 ± 0.4 $M^{-1}\ s^{-1}$ agree with Benson's[20] and Golden's[21] suggestions that for H-atom transfer involving polyatomic radicals log ($A/(M^{-1}\ s^{-1})$) should be no lower than 8 to 9. Hendry et al. assigned log A for abstraction of primary H in alkanes as 9.0 and from secondary alkanes 9.2 whereas for compounds containing heteroatoms in which resonance effects involving p electrons appeared to be small they used log A = 8.7 and neglected differences between primary, secondary, and tertiary CH bonds. Our result of 8.6 agrees very well with their estimated value.

The log A for abstraction by a CCl_3 radical is higher than for abstraction by a CH_3 radical, 8.6 as compared to 8.0 found for CH_3 in the gas phase.[22]

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(11) Z. B. Alfassi and L. Feldman, *Int. J. Chem. Kinet.*, **13**, 517 (1981).

(12) H. C. Van Beek and H. J. van der Stoep, *Recl. Trav. Chim. Pays-Bas*, **97**, 279 (1978).

(13) R. Koster and K. D. Asmus, *Z. Naturforschung.*, *B*, **26**, 1104 (1971).

(14) M. G. Katz, G. Baruch, and L. A. Rajbenbach, *Int. J. Chem. Kinet.*, **8**, 131, 509 (1976).

(15) H. Watts, B. J. Adler, and J. H. Hildebrand, *J. Chem. Phys.*, **23**, 659 (1955).

(16) H. Paul, *Int. J. Chem. Kinet.*, **11**, 495 (1979).

(17) M. L. White and R. R. Kuntz, *Int. J. Chem. Kinet.*, **3**, 127 (1971); P. B. Wampler and R. R. Kuntz, *ibid.*, **3**, 283 (1971).

(18) S. W. Benson, A. N. Bose, and P. Nangia, *J. Am. Chem. Soc.*, **85**, 1388 (1963).

(19) A. A. Herod, *Chem. Commun.*, 891 (1968).

(20) S. W. Benson, "Thermochemical Kinetics", Wiley, New York, 1968.

(21) D. M. Golden, *Symp. (Int.) Combust.*, [*Proc.*], *14th*, 121 (1973).

(22) P. Gray and A. A. Herod, *Trans. Faraday Soc.*, **64**, 2723 (1968).

(23) N. E. Bibler, *J. Phys. Chem.*, **75**, 24 (1971).