

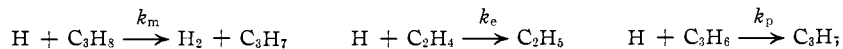
[CONTRIBUTION FROM THE RADIATION LABORATORY, CONTINENTAL OIL COMPANY, PONCA CITY, OKLAHOMA]

Free Radical Reactions Initiated by Ionizing Radiations. I. Arrhenius Parameters for the Reactions of Hydrogen Atoms with Propane, Ethylene and Propylene

BY KANG YANG

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The presence of ethylene or propylene in the gamma radiolysis of propane reduces the rate of formation of hydrogen. The extent of this inhibition depends both on radiolysis temperature and olefin concentration. This can be explained quantitatively by assuming the occurrence of the following reactions:

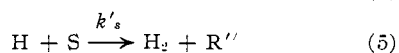
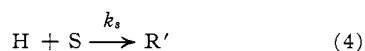
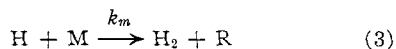
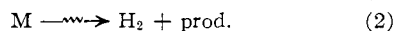
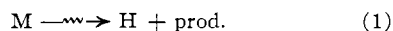


The relative rates $k_m/k_e = 1.1 \exp(-4.4 \times 10^3/RT)$; $k_m/k_p = 1.4 \exp(-4.8 \times 10^3/RT)$; and $k_e/k_p = 1.3 \exp(-0.4 \times 10^3/RT)$ are determined based on this radical mechanism.

Introduction

In the present series of investigations we attempt to determine the rate constants of the reactions involving hydrogen atoms produced by the gas phase radiolysis of saturated hydrocarbons. Quantitative treatment of many radiolysis mechanisms demands such information, but presently available experimental results seem to be limited and conflicting.¹⁻³

The method to be employed here was first developed by Back⁴ and Hardwick⁵ and utilizes the experimental observation⁶ that the presence of a scavenger, S, in the radiolysis of a compound M, often diminishes the rate of formation of hydrogen



The steady state approximation gives a relation

$$r_0 - r_s = r_1 \frac{k_s[\text{S}]}{k_m[\text{M}] + (k_s + k'_s)[\text{S}]} \quad (\text{E-1})$$

Here, r_0 and r_s denote, respectively, the rates of formation of hydrogen molecules in the absence and presence of scavenger, while r_1 represents the rate of formation of hydrogen atoms; and the k 's are the respective rate constants. Hardwick⁵ rearranged (E-1) to the form

$$\frac{1}{r_0 - r_s} = \frac{1}{r_1} \left(\frac{k_m}{k_s} \right) \frac{[\text{M}]}{[\text{S}]} + \frac{1}{r_1} \left(1 + \frac{k'_s}{k_s} \right) \quad (\text{E-2})$$

and determined the rate constant ratio for various liquid phase reactions by plotting $(r_0 - r_s)^{-1}$ against $[\text{M}]/[\text{S}]$. By using essentially the same equation, Back⁴ and Yang and Gant⁷ investigated some hydrogen atom reactions in the gas phase radiolysis of saturated hydrocarbons.

At present the support of the mechanism, (1) to (5), comes from two sources.^{4,5,7} First, the depend-

(1) E. W. R. Steacie, "Atomic and Free Radical Reactions," Reinhold Publishing Corporation, New York, N. Y., 1954.

(2) A. F. Trotman-Dickenson, "Gas Kinetics," Butterworths Scientific Publications, London, 1955.

(3) S. W. Benson, "The Foundations of Chemical Kinetics," McGraw-Hill Book Company, New York, N. Y., 1960.

(4) R. A. Back, *J. Phys. Chem.*, **64**, 124 (1960).

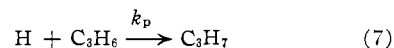
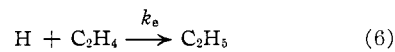
(5) T. J. Hardwick, *ibid.*, **65**, 101 (1961).

(6) For example see: L. M. Dorfman, *ibid.*, **62**, 29 (1958).

(7) K. Yang and P. L. Gant, *ibid.*, (in press).

ence of the rate on the scavenger concentration is in agreement with (E-2), and, second, the resulting ratio of the rate constants is reasonable. Another test is to investigate the dependence of the ratio on temperature. Since rate constants for gas phase reactions are usually well represented by the Arrhenius equation, $k = A \exp(-E^*/RT)$, one should obtain a straight line when $\ln(k_m/k_s)$ is plotted against $1/T$. The present experiments confirm this prediction.

As the compound M to be radiolyzed, propane was chosen. It is the simplest commercially available saturated hydrocarbon that does not require elaborate purification for the present purpose. Ethylene and propylene were selected as scavengers. The main reason for this choice is that the relative rates of the two reactions



are of kinetic interest but available information is conflicting.⁸⁻¹⁰

The determination of k'_s/k_s using (E-2) requires the estimation of intercepts. Because of this, the resulting ratio was inaccurate; however, this ratio did not exceed 0.08 in the present experiment. If we neglect k'_s/k_s compared with unity, (E-2) may be rearranged to give

$$r_s = \frac{k_m}{k_s} \frac{[\text{M}]}{[\text{S}]} (r_0 - r_s) + r_2 \quad (\text{E-3})$$

where $r_2 (= r_0 - r_1)$ denotes the rate of reaction 2. In this form, the extrapolation of rate data to infinite concentration of scavenger (for the estimation of r_1) is not required in obtaining the desired ratio, k_m/k_s .

In the present experiment, both *n*- and *iso*-propyl radicals are likely to form in reactions 3 and 7. With the method we employed, it was not possible to distinguish this situation. Hence, k_m and k_p reported here are composite rate constants.

Experimental

Phillips' research grade propane was degassed by repeated evacuation at liquid nitrogen temperature, then subjected

(8) P. E. Allen, H. W. Melville and J. C. Robbs, *Proc. Roy. Soc. (London)*, **A128**, 311 (1953).

(9) B. de B. Darwent and R. Roberts, *Discussion Faraday Soc.*, **14**, 55 (1953).

(10) A. B. Callear and J. C. Robbs, *Trans. Faraday Soc.*, **51**, 638 (1955).

to a three-stage bulb-to-bulb distillation, each time retaining the middle third. Phillips' research grade ethylene and propylene were degassed similarly but subjected to the distillation only once. Reaction vessels (Pyrex, 140 cc.) equipped with capillary constrictions and break-off seals were charged with 50 cm. Hg of propane and varying amounts of scavengers (at room temperature). A thermocouple-controlled furnace completely enclosed the reaction vessel. The vessel used to measure reaction temperature was the same as the one used in obtaining rate data except that the former was equipped with a thermocouple well. During a single experiment lasting up to 40 minutes, temperature did not fluctuate more than $\pm 2^\circ$. About 1×10^4 curies of Co^{60} were used to initiate reaction. Energy input rate, measured by using an ethylene dosimeter,⁷ was 1.4×10^{-3} e.v. per hour per molecule of propane.

After irradiation, samples were connected directly to gas chromatographic equipment through break-off seals. A silica gel column at room temperature with argon carrier was used in the determination of hydrogen concentrations (10^{-2} – 10^{-3} per cent). Other details of the experimental procedures have been described previously.⁷

Results

Table I summarizes typical experimental results showing decrease in the rate of hydrogen formations with increasing scavenger concentration. In all experiments, the ratio, $[\text{H}_2]/[\text{C}_3\text{H}_8]$, did not exceed 4.5×10^{-5} . The maximum fraction of propane decomposed is probably the same order of magnitude.

TABLE I

HYDROGEN FORMATION IN THE RADIOLYSIS OF THE C_3H_8 - C_3H_6 SYSTEM AT 201°

$[\text{C}_3\text{H}_6]/[\text{C}_3\text{H}_8]^a$ $\times 10^2$	Irrad. time (min.) ^b	$[\text{H}_2]/[\text{C}_3\text{H}_8]$ $\times 10^5$	Rate ^c $\times 10^5$
0.00	30.0	4.48	8.96
1.19	40.0	3.52	5.28
2.38	40.0	2.80	4.20
4.72	40.0	2.32	3.48
5.91	40.0	2.16	3.24

^a Propane pressure at room temperature = 500–501 mm. Energy input rate = 1.4×10^{-3} e.v. per hour per molecule of propane. ^c $[\text{H}_2]/[\text{C}_3\text{H}_8]/\text{hr}$.

The data in Table I were in good agreement with (E-3). From least square treatment, we obtained

$$r_0 = (9.5 \pm 0.2) \times 10^{-3} \frac{[\text{M}]}{[\text{S}]} + (2.3 \pm 0.1) \times 10^{-5} \quad (\text{E-4})$$

Deviations shown in (E-4) (and in subsequent equations) are standard deviations.

The rate constant ratios obtained from similar experiments at various temperatures are summarized in Table II. Arrhenius plots obtained by using the data in Table II were good straight lines. The equations resulting from least square treatment were:

$$\log \frac{k_m}{k_e} = (0.06 \pm 0.07) - (4400 \pm 100) \frac{1}{4.58T} \quad (\text{E-5})$$

$$\log \frac{k_m}{k_p} = (0.15 \pm 0.05) - (4800 \pm 100) \frac{1}{4.58T} \quad (\text{E-6})$$

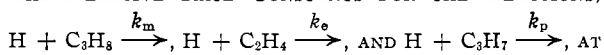
Hence

$$\log \frac{k_e}{k_p} = (0.09 \pm 0.09) - (400 \pm 100) \frac{1}{4.58T} \quad (\text{E-7})$$

Unscavenged rate r_0 and completely scavenged rate r_2 are of importance in discussing radiolysis mechanisms.⁶ Neither of these rates showed any temperature dependence (56 – 240°). Since the rate is expressed in $[\text{H}_2]/[\text{C}_3\text{H}_8]$ per hour and energy input \dot{E} in e.v. per hour per molecule, the customarily

TABLE II

THE RELATIVE RATE CONSTANTS FOR THE REACTIONS,



VARIOUS TEMPERATURES

Temp. ($^\circ\text{K}$.)	$(k_m/k_e) \times 10^3$	Temp. ($^\circ\text{K}$.)	$(k_m/k_p) \times 10^3$
329	1.4	330	0.96
334	1.5	352	1.4
383	3.5	403	3.6
403	4.9	474	8.7
415	5.6	483	8.9
450	10.0	490	10.5
474	9.5		
485	12.3		
503	14.2		
513	15.5		

employed G values (molecules/100 e.v.) may be obtained from the relation: $G = \text{rate} \times 100/\dot{E}$. The resulting G values for r_0 and r_2 were, respectively, 6.4 and 1.6. These values may be compared with Back's data,⁴ obtained by investigating propane radiolysis (among others) at very low conversion and at ambient temperature. His relative rates (when recalculated to give $G(\text{H}_2)$ of 1.2 in ethylene radiolysis) give 6.3 and 1.6 for $G(\text{H}_2)$ corresponding to r_0 and r_2 in good agreement with our results.

Discussion

The present result, $k_e/k_p = 1.3 \exp(-400/RT)$, shows that, because of the lower activation energy, hydrogen atoms attack propylene more readily than ethylene at temperatures lower than $\sim 520^\circ$. This is in disagreement with the result of Darwent and Roberts,⁹ who investigated the photolysis of H_2S in the presence of ethylene or propylene at two different temperatures and reported that $k_e/k_p = 0.1 \exp(+0.9 \times 10^3/RT)$. The source of this discrepancy is not apparent.

From (E-7), we estimate $k_e/k_p = 0.7$ at 25° . This is compatible with the result of thermal method¹⁰ ($=0.3$ at 31°), which employs platinum wire to measure heat liberated by atomic recombinations but not with the result of molybdenum oxide method⁸ ($=3.1$ at 18°). For this reason, the rate constant, $k_p = 4.8 \times 10^{11}$ mole⁻¹ cc. sec.⁻¹ at 31° obtained by the thermal method, is used below to estimate absolute Arrhenius parameters.

The present method gives only relative rate constants. To obtain individual rate constants from these results, some additional information is needed. We have taken a recent result,¹¹ $E^* = 1.5$ kcal./

TABLE III

ARRHENIUS PARAMETERS, A (MOLE⁻¹ CC. SEC.⁻¹) AND E^* (KCAL./MOLE) FOR SOME HYDROGEN ATOM REACTIONS

Reactions	Log A		E	
	This work	Lit. ^a	This work	Lit. ^a
$\text{H} + \text{C}_2\text{H}_5 \rightarrow \text{C}_2\text{H}_5$	12.9	13.5	1.9	4.1
$\text{H} + \text{C}_3\text{H}_8 \rightarrow \text{C}_3\text{H}_7$	12.8	14.4	1.5	5.0
$\text{H} + \text{C}_3\text{H}_8 \rightarrow \text{H}_2 + \text{C}_3\text{H}_7$	13.0	(14.5) ^b	6.3	(7.2) ^b

^a Darwent and Roberts, ref. 9. ^b These values are for the reaction of D atoms with propane.

mole for the $\text{H}-\text{C}_6\text{H}_6$ reaction, and adjusted the A -factor for this reaction to give $k_p = 4.8 \times 10^{11}$ mole $^{-1}$ cc. sec. $^{-1}$ at 31° . The result thus obtained was used to estimate the Arrhenius parameters summarized in Table III, where the results in reference 9 are also included for comparison. The present

values for both A and E are lower in all three reactions. The source of this discrepancy is not clear.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE UNIVERSITY OF MICHIGAN, ANN ARBOR, MICHIGAN]

Ion Association in Polyvalent Symmetrical Electrolytes. IV. The Conductance of MnSO_4 and MnBDS in Dioxane-Water Mixtures

BY GORDON ATKINSON¹ AND CALVIN J. HALLADA²

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The conductance of $\text{Mn } m$ -benzene disulfonate (MnBDS) has been measured in mixtures from 0 to 40% dioxane; and MnSO_4 has been studied from 0 to 25% dioxane. The data are analyzed using the Fuoss-Onsager theory and K_A , Λ^0 and a_j parameters obtained. As was found in the previous work on these salts in methanol-water mixtures, MnBDS is far less associated in water than MnSO_4 . a_j and the Walden product ($\Lambda^0\eta$) are constant for both salts over the solvent range examined and the same as found in the methanol-water mixtures. However, the K_A 's found in the dioxane-water mixtures are uniformly lower than those found in the methanol-water mixtures of the same dielectric constant. It also is found that the $\log K_A$ vs. $1/D$ plot for only MnSO_4 in dioxane-water mixtures is in very good agreement with the Fuoss-Bjerrum theory of ion-pairing. Various speculations on the solvation of the ions involved are advanced to tentatively explain these results.

Recent work on the conductance of high-charge electrolytes³⁻⁵ has demonstrated the existence of 2-2 salts that are only very slightly associated in water. These substances, the Cu(II) and Mn(II) salts of m -benzene disulfonic acid and the Cu(II) salt of 4,4'-biphenyldisulfonic acid follow the Fuoss-Onsager theoretical predictions exactly and yield very reasonable values of the conductance parameters Λ^0 and a_j . One of these salts MnBDS has been examined in methanol-water mixtures from 0 to 100% methanol; and as a comparison, MnSO_4 was examined in the same solvent mixtures. It was found that in the range 0 to 0.25 mole fraction methanol both salts exhibited a constant value of a_j (the ion size parameter) and the Walden product, $\Lambda^0\eta$. In addition, the plots of $\log K_A$ vs. $1/D$ were linear for both salts in this range. Unfortunately, solubility problems prevented the extension of the measurements much past this range for MnSO_4 . For MnBDS , where the measurements could be made to 100% methanol, it was found that a_j and $\Lambda^0\eta$ deviated strongly from the low methanol concentration values when X_{MeOH} was greater than 0.25. It also was shown that the association constants in this high methanol content range were not consistent with the low range values. All of these deviations were tentatively correlated with the extreme deviations of the methanol-water solvent mixtures from ideality.

In an attempt to further clarify this problem and to further determine the association of these salts, measurements have been made in dioxane-water mixtures covering the same dielectric constant range.

(1) Department of Chemistry, University of Maryland, College Park, Maryland.

(2) Union Carbide Nuclear Corporation, Tuxedo, New York.

(3) G. Atkinson, M. Yokoi and C. J. Hallada, *J. Am. Chem. Soc.*, **83**, 1570 (1961).

(4) C. J. Hallada and G. Atkinson, *ibid.*, **83**, 3759 (1961).

(5) M. Yokoi and G. Atkinson, *ibid.*, **83**, 4367 (1961).

Experimental

The preparation, purification and analysis of the Mn(II) salts have been described previously⁴ as have the apparatus and modus operandi.³ All solutions were made up by weight in flask-type conductance cells. Pycnometric densities were used for conversion to the molarity scale. The dioxane was purified by the standard procedures⁶; and the physical constants of the dioxane-water mixtures used in the calculations were those given by Fuoss.⁷ Hydrolysis corrections were not used because their calculated size fell within the experimental errors of Λ determination.

Data Treatment.—Table I gives the equivalent conductance and concentration data for the two salts in the various solvent mixtures. The phoreograms of the two salts in the different solvent mixtures are so similar to those shown previously⁴ as to make their portrayal superfluous.

For the treatment of the data the Fuoss-Onsager equation in the form for associated electrolytes was used. We again have ignored the viscosity correction which has been proposed by Fuoss since its contribution to 2-2 salt conductances is unknown.

$$\Lambda = \Lambda^0 - S(C\alpha)^{1/2} + E(C\alpha) \log(C\alpha) + \frac{J(C\alpha) - K_A(C\alpha)f_{\pm}^2\Lambda}{J(C\alpha) - K_A(C\alpha)f_{\pm}^2\Lambda} \quad (1)$$

where the symbols are explained in references 4 and 7, (particularly 4, for 2-2 salt treatment).

For the actual analysis of the association we have adopted the Fuoss "y-x" method and have used the Debye-Hückel extended equation to calculate the activity coefficients, f_{\pm} . The calculation has been programmed for the IBM 704 computer so that maximum utilization of data can be achieved. Fuoss defines

$$\Lambda' = \Lambda + SC_i^{1/2} - EC_i \log C_i \quad (2)$$

$$\Delta\Lambda = \Lambda' - \Lambda^0 \quad (3)$$

$$y = \Delta\Lambda/C_i \quad (C_i = \alpha C) \quad (4)$$

and

$$x = f_{\pm}^2\Lambda \quad (5)$$

Then

$$y = J - K_A x \quad (6)$$

The computer first evaluates an approximate α from

$$\alpha_1 = \frac{\Lambda}{\Lambda^0 - S(\Lambda/\Lambda^0)^{1/2}C^{1/2}} \quad (7)$$

(6) C. A. Kraus and R. A. Vinge, *ibid.*, **56**, 513 (1934).

(7) R. M. Fuoss and F. Accascina, "Electrolytic Conductance," Interscience Publishers, Inc., New York, N. Y., 1959.