

tities in the experimental range used. The calculated values are also found to be temperature independent and agreement exists to within 0.12 kcal./mole for  $\Delta H^\circ(\text{II})$  and 0.24 gibbs/mole for  $\Delta S^\circ(\text{II})$ . Inasmuch as the entropy of  $\text{H}_2$  is known very accurately from statistical mechanical calculations, the difference in  $S^\circ$  values for  $\text{C}_3\text{H}_6$  and  $\text{C}_3\text{H}_8$  can be calculated to that accuracy. As the A.P.I. values are based in part on assignments of internal barriers of methyl groups in  $\text{C}_3\text{H}_8$  and  $\text{C}_3\text{H}_6$  which are different in the two compounds, the remarkable agreement between the observed value (present work) and calculated value (A.P.I. data) of the difference in  $5^\circ$  ( $\text{C}_3\text{H}_6$ - $\text{C}_3\text{H}_8$ ) shows that the magnitudes of these barriers are probably accurate to within 10%.

Kistiakowsky and Nickle<sup>10</sup> have measured the heat of the dehydrogenation reaction  $\text{C}_3\text{H}_8 \rightleftharpoons \text{C}_3\text{H}_6 + \text{H}_2$  as  $\Delta H_{616}^\circ = 30.5 \pm 1.2$  kcal./mole from observations of equilibrium compositions using reduced chromic hydroxide as a catalyst. This value agrees well with our own more precise value  $\Delta H^\circ(\text{II}) = 30.75 \pm 0.40$  kcal./mole.

In view of the precisely known thermodynamic data for  $\text{I}_2$  and  $\text{HI}$ , it is apparent that the present simple technique makes it possible to determine with quite high precision differences in the values of enthalpies and entropies of any pair of suitable hydrocarbon and olefin.

(10) G. B. Kistiakowsky and A. G. Nickle, *Discussions Faraday Soc.*, **10**, 175 (1951).

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, UNIVERSITY OF SOUTHERN CALIFORNIA, LOS ANGELES 7, CALIFORNIA]

## The Kinetics of Dehydrogenation of Propane by Iodine Vapor and the Heat of Formation of the Isopropyl Radical<sup>1a</sup>

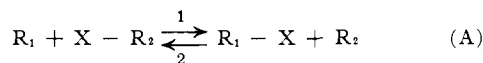
BY PRAKASH S. NANGIA<sup>1b</sup> AND SIDNEY W. BENSON<sup>1c</sup>

RECEIVED FEBRUARY 10, 1964

The kinetics of the gas-phase dehydrogenation reaction  $\text{C}_3\text{H}_8 + \text{I}_2 \rightleftharpoons 2\text{HI} + \text{C}_3\text{H}_6$  has been studied manometrically from 308 to 340°. Assuming that the mechanism proceeds by the H atom abstraction,  $\text{I} + \text{C}_3\text{H}_8 \xrightleftharpoons[2]{1} \dot{\text{i}}\text{-C}_3\text{H}_7 + \text{HI}$ , it is possible to obtain Arrhenius parameters for  $k_1$ . From these and the assumption that  $E_2 = 1$  kcal., it is deduced that the secondary C-H bond in  $\text{C}_3\text{H}_8$  has a dissociation energy of 94.5 kcal. For the *i*-Pr radical,  $\Delta H_f^\circ(\dot{\text{i}}\text{-Pr})$  is calculated as 17.6 kcal./mole. Both values have an estimated uncertainty of  $\pm 1$  kcal./mole. I atom attack on the primary C-H bonds is estimated to contribute less than 15% to the over-all rate.

### Introduction

The accurate determination of the heats of formation of radicals more complex than diatomics is extremely difficult.<sup>2</sup> The most precise values available today are almost all derived from kinetic studies<sup>3</sup> of systems in which relative or absolute rate constants may be measured for abstraction reactions of the type



Even where it is possible to measure  $k_1$  and its activation energy  $E_1$ , it is not possible usually to do the same for the back reaction 2 independently. In consequence, the quantity which is desired, the bond dissociation energy  $D(\text{R}_2-\text{X})$  from which the  $\Delta H_f^\circ(\text{R}_2)$  can be obtained, can only be measured if  $E_2$ , the activation energy for the back reaction, is known.

In the kinetic studies of halogenation reactions where  $\text{R}_1$  is a halogen atom and  $\text{X}$  is either an H atom or a halogen atom, the activation energy for the back reaction is generally assumed to be zero or very small. Thus the exothermic abstraction reactions  $\text{H} + \text{I}_2$  and  $\text{H} + \text{HI}^3$  have zero activation energies while  $\text{H} + \text{HBr}$  and  $\text{H} + \text{Br}_2^4$  have about 1 kcal. It has been generally assumed that the exothermic reactions of alkyl radicals with  $\text{I}_2$  have activation energies in the range 0 to 0.5

kcal. and the best value quoted today for the C-H bond dissociation energy of  $\text{CH}_4$  is based on this assumption.<sup>5</sup> We have found in our own studies of the reactions of organic radicals with both  $\text{HI}$  and  $\text{I}_2$  that the differences in activation energies between  $\text{R} + \text{HI}$  and  $\text{R} + \text{I}_2$  are about  $1 \pm 0.5$  kcal.<sup>6,7</sup> If the assumption that  $\text{R} + \text{I}_2$  has essentially zero activation energy is correct, then the reactions of I atoms with organic molecules lend themselves very well to the fairly precise study of bond dissociation energies. The largest error in these studies is that concerned with the magnitude of the activation energy for the abstraction reaction  $\text{R} + \text{I}_2$ .

From such studies we have been able to obtain what we feel are the most reliable values for the bond dissociation energies in a large number of organic molecules<sup>6-8</sup> in good agreement with values obtained by less precise methods. Among the simple alkyl radicals, there now seems to be good agreement on the C-H bonds in  $\text{CH}_4$ ,<sup>4,6b,9</sup>  $\text{C}_2\text{H}_6$ ,<sup>10,11</sup> and the tertiary C-H bond in isobutane.<sup>7,12</sup> However, there appear to be no direct measurements of the secondary C-H bond in  $\text{C}_3\text{H}_8$  and there has been some controversy on its magnitude.<sup>13</sup>

(5) H. C. Anderson and G. B. Kistiakowsky, *J. Chem. Phys.*, **11**, 6 (1943).

(6) (a) H. E. O'Neal and S. W. Benson, *ibid.*, **36**, 2196 (1962); (b) M. C. Flowers and S. W. Benson, *ibid.*, **38**, 882 (1963).

(7) H. Teranishi and S. W. Benson, *J. Am. Chem. Soc.*, **85**, 2887 (1963).

(8) S. W. Benson, A. N. Bose, and P. S. Nangia, *ibid.*, **85**, 1388 (1963).

(9) H. C. Anderson and E. R. van Artsdalen, *J. Chem. Phys.*, **12**, 479 (1944).

(10) D. B. Hartley and S. W. Benson, *ibid.*, **39**, 132 (1963).

(11) H. C. Anderson, G. B. Kistiakowsky, and E. A. van Artsdalen, *ibid.*, **10**, 305 (1942); see also ref. 5.

(12) G. C. Fettes, J. H. Knox, and A. F. Trotman-Dickenson, *J. Chem. Soc.*, **A177** (1960).

(13) T. L. Cottrell, "The Strengths of Chemical Bonds," 2nd Ed., Butterworths Scientific Publications, London, 1958, p. 182.

(1) (a) This work has been supported by grants from the U. S. Atomic Energy Commission and the National Science Foundation; (b) this work constitutes part of the Ph.D. Thesis of P. S. Nangia, 1964; (c) Stanford Research Institute, Menlo Park, Calif., to whom requests for reprints should be addressed.

(2) See M. Szwarc, *Chem. Rev.*, **47**, 75 (1950), for a discussion of some of the difficulties.

(3) J. H. Sullivan, *J. Chem. Phys.*, **30**, 1292, 1577 (1959).

(4) M. Jost, *Z. physik. Chem.*, **B3**, 95 (1929).

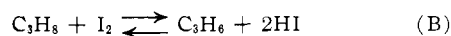
TABLE I  
 RATE CONSTANTS DATA FOR THE REACTION  $C_3H_8 + I_2$ 

Run	Temp., °K.	$(C_3H_8)_0$	$(I_2)_0$	Intercept $(I_n) \times 10^{-3}$ , (min.) <sup>1/2</sup>	Slope $(S) \times 10^{-3}$ , min.	$3 + \log$ $ K_{I_2}^{1/2}$ (mm.) <sup>1/2</sup> p	$\log [K \text{ (mm.)}]$	$\log [k_1$ (1./mole sec.)]	$2 + \log [k_2^a$ (1./mole sec.)]
10	612.8	17.48	5.66	0.48	0.30	0.664	1.015	2.459	1.310
20	613.0	24.41	4.75	.50	.53	.665	1.027	2.441	1.053
21	613.1	20.39	8.29	.49	.55	.665	1.027	2.450	1.037
26	603.0	25.51	4.75	.90	1.25	.558	.860	2.285	0.840
28	605.0	26.11	4.95	.75	1.18	.580	.907	2.344	.819
29	604.5	22.87	7.79	.81	1.30	.574	.890	2.316	.794
30	600.0	20.61	6.32	.98	0.84	.524	.807	2.280	1.066
31	601.5	42.55	6.27	.91	.77	.541	.833	2.296	1.077
32	600.3	64.44	6.33	1.10	.85	.528	.813	2.226	1.056
33	600.3	44.19	22.19	1.03	.69	.528	.813	2.254	1.144
34	599.2	32.17	22.09	1.12	1.05	.516	.796	2.230	0.977
35	597.8	22.02	22.23	1.18	1.21	.500	.771	2.221	.940
36	601.2	32.39	12.70	1.18	1.04	.538	.830	2.186	.949
38	593.0	41.91	10.61	1.58	2.01	.446	.690	2.145	.797
39	593.2	37.77	23.06	1.58	1.85	.448	.692	2.144	.831
40	594.0	41.89	23.44	1.52	1.85	.458	.707	2.161	.818
14	593.5	25.22	4.83	1.50	1.29	.452	.694	2.165	.987
16	593.5	25.70	4.86	1.48	1.16	.452	.697	2.168	1.029
42	580.0	52.01	10.74	3.60	5.14	.296	.462	1.928	0.607
43	583.1	45.61	11.45	3.30	4.30	.332	.519	1.943	.639
44	581.5	36.66	18.25	3.10	3.95	.314	.491	1.976	.694
45	584.1	36.97	18.59	2.75	4.20	.344	.537	2.000	.623
22	581.0	22.32	7.31	3.30	4.95	.308	.470	1.955	.616

<sup>a</sup>  $k_6 = 1/KS$ . <sup>b</sup>  $K_{I_2}$  values were calculated from thermodynamic data given in Table II.

Kinetic studies of the gas phase reaction of  $C_3H_8 + I_2$  at temperatures near  $300^\circ$  are capable of yielding values for the (*i*-Pr-H) bond dissociation and these are reported on in the present paper. The thermodynamics study of this dehydrogenation reaction has been reported earlier.<sup>14</sup>

The over-all reaction is



### Experimental

The materials used, the apparatus, and the technique were as reported earlier.<sup>14</sup> In the present investigation, only pressure measurements were made for the kinetic runs carried out in the packed vessel as before.

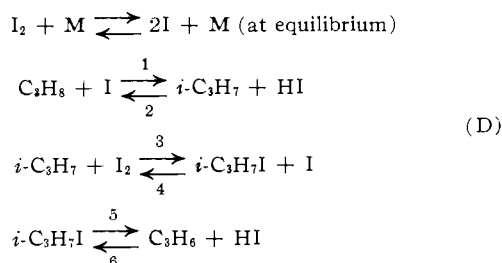
The stoichiometry for the reaction has also been established in this previous study. As the steady-state concentration of isopropyl iodide is justified *a posteriori* to be negligibly small, the observed pressure increase  $\Delta p$  at any time is equal to loss of either  $I_2$ , or to the loss of  $C_3H_8$ . The following relations are thus valid.

$$(C_3H_8)_t = (C_3H_8)_0 - [(I_2)_0 - (I_2)_t] = (C_3H_8)_0 - \Delta p \quad (C)$$

$$(C_3H_6)_t = (I_2)_0 - (I_2)_t = \Delta p$$

### Mechanism and Treatment of Data

Based on previous studies on the reactions of HI with  $RI$ ,<sup>10</sup> of the addition of HI to olefins,<sup>15</sup> and the principle of detailed balancing, the following steps can be supposed to occur in the dehydrogenation of  $C_3H_8$  by  $I_2$



In the preceding mechanism, termination processes like  $i\text{-}C_3H_7 + I \rightarrow$  products, and  $2C_3H_7 \rightarrow$  products, have been neglected, for it can be shown that the ratio<sup>16</sup>  $(i\text{-}C_3H_7)/(I) \ll 1$ . Further, I atoms are in equilibrium with  $I_2$ . This is a common feature in all iodide studies.

On application of the quasi-stationary state hypothesis for  $RI$  and  $R$  in scheme D, the following rate law for the disappearance of  $I_2$  can be deduced

$$S' = -\frac{d(I_2)}{dt} = \frac{k_1 K_{I_2}^{1/2} (C_3H_8) (I_2)^{1/2} (1 - B)}{1 + \frac{k_2}{k_3} \frac{(HI)}{(I_2)} \left[ 1 + \frac{k_4}{k_5} (I) \right]} \quad (1)$$

where  $K_{I_2}$  is the equilibrium constant for the  $I_2$ -I equilibrium;  $B = (C_3H_6)(HI)^2/K(C_3H_8)(I_2)$  is a correction term for the back reaction, and  $K$  is the measured equilibrium constant for the over-all reaction (B). The above expression (1) may be recast in a useful form by using the relations,  $S \equiv -d(I_2)^{1/2}/dt = -1/2(I_2)^{1/2} \times d(I_2)/dt$ ;  $(I) = K_{I_2}^{1/2}(I_2)^{1/2}$ ; and  $(k_2 k_4)/(k_3 k_5) \equiv (k_1/k_6)/K$ .

(16) From scheme D, this ratio is given by

$$\frac{(i\text{-}C_3H_7)}{(I)} = \frac{1}{k_3(I_2)\Phi} \left\{ k_1(C_3H_8) + k_4 \times \frac{\left[ \frac{k_1}{k_6} K_{I_2}^{1/2} (C_3H_8) (I_2)^{1/2} + (C_3H_6)(HI)\Phi \right]}{K_{5,6} \left[ \Phi + \frac{k_1}{k_6} \frac{K_{I_2}^{1/2} (HI)}{(I_2)^{1/2}} \right]} \right\}$$

where  $\Phi = 1 + [k_2(HI)/k_3(I_2)]$ . Using approximately, if not accurately, known values of the various quantities involved, the second term in brackets can be shown to be  $\leq K_{I_2}^{1/2}(k_4/k_3)k_1(C_3H_8)(I_2)^{1/2}$  and the ratio,  $(C_3H_7)/(I) \leq [k_1(C_3H_8)/k_3(I_2)\Phi][1 + K_{I_2}^{1/2}(k_4/k_3)(I_2)^{1/2}]$  under the experimental conditions, and further  $\Phi \approx 1.02 \sim 1.04$  and  $K_{I_2}^{1/2}K_{4,5}(I_2)^{1/2} = 8$  to 16. Since  $k_1/k_3 \approx (10^{11} \times 10^{-25/6})/10^1 \ll 1$ , the over-all desired ratio is  $\ll 1$ .

(14) P. S. Nangia and S. W. Benson, *J. Am. Chem. Soc.*, **86**, 2770 (1964).

(15) A. N. Bose and S. W. Benson, *J. Chem. Phys.*, **38**, 878 (1963).

$$Z \equiv \frac{(C_3H_8)(1-B)}{2S} = \frac{1}{k_1 K_{I_2}^{1/2}} + \frac{1}{k_6 K (I_2)^{1/2}} + \frac{1}{k_1 K_{I_2}^{1/2}} \frac{k_2}{k_3} \frac{(HI)}{(I_2)^{1/2}} \quad (2)$$

Or by regrouping terms

$$Z = \frac{1}{k_1 K_{I_2}^{1/2}} \left[ 1 + \frac{k_2}{k_3} \frac{(HI)}{(I_2)^{1/2}} \right] + \frac{1}{k_6 K (I_2)^{1/2}} \quad (3)$$

Now our previous experiences with a variety of radical systems have shown that  $(k_2/k_3)$  is usually  $< 0.25$  so that in the first 15% of reaction, the term in brackets of eq. 3 does not deviate from unity by more than 8–12%. Consequently, if the last term on the right hand side of eq. 3 is significant, then a plot of  $Z$  vs.  $(HI)/(I_2)^{1/2}$  should give a straight line over this early position of the reaction. From the slope and intercept of this line it is

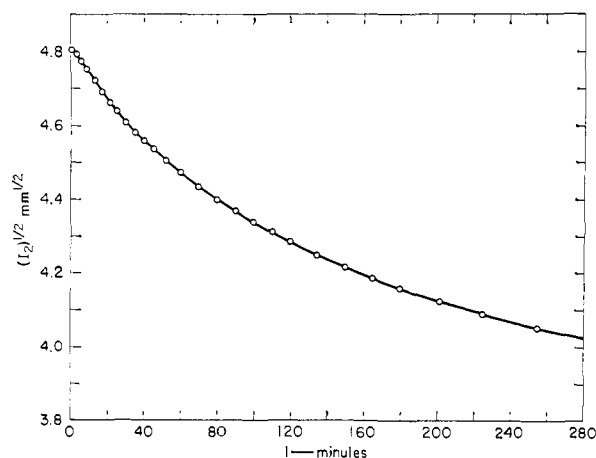


Fig. 1.—Plot of  $(I_2)^{1/2}$  vs. time: ordinate,  $(I_2)^{1/2}$  (mm.) $^{1/2}$ ; abscissa,  $t$ , min.

possible to get values for  $k_1/K_{I_2}^{1/2}$  and  $k_6K$ . Once these are obtained, an analytical fit of the data to eq. 3 can be made to get the best values of  $k_2/k_3$ .<sup>7</sup> Alternatively, since  $K$  is measured independently and  $k_6$  is known also from independent measurements,<sup>17</sup> it is possible to plot  $[Z - (HI)/k_6K(I_2)^{1/2}]$  vs.  $(HI)/(I_2)^{1/2}$  to get a straight line from where slope and intercept  $k_1K_{I_2}^{1/2}$  and  $k_2/k_3$  are independently calculable.

### Results and Discussion

The kinetic studies were carried out in the temperature range 580 to 613°K. and the results of 22 runs are given in Table I. While the composition was varied extensively, the temperature range is limited, for at lower temperatures, the reaction becomes too slow while at higher temperatures the surface pyrolysis of  $C_3H_8$  occurred in the packed vessel.<sup>14</sup> It was also found expedient to plot  $(I_2)$  vs.  $t$  and use the measured slope  $S' = d(I_2)/dt$  in expression 2. This is because  $S'$  is larger than  $S$  [ $S' = 2S(I_2)^{1/2}$ ] and could be more accurately and precisely measured. The slopes were measured<sup>18</sup> and found reproducible to within  $\pm 1\%$ .

A typical plot of  $(I_2)^{1/2}$  vs.  $t$  (for run 39) is shown in Fig. 1 and has a sigmoid-shape curvature with a small

(17) A. N. Bose and S. W. Benson, *J. Chem. Phys.*, **37**, 1081 (1962).

(18) C. J. Hochanadel, *J. Chem. Educ.*, **39**, 299 (1962), has described the technique which was improved to the extent of giving the above reproducibility.

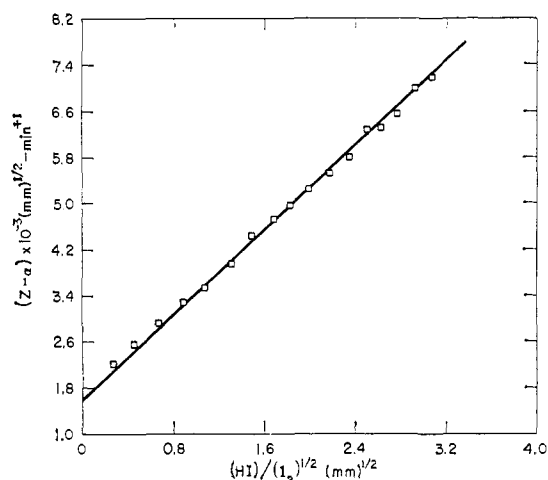


Fig. 2.—Plot of  $(Z - \alpha)$  vs.  $(HI)/(I_2)^{1/2}$ : ordinate,  $(Z - \alpha) \times 10^{-3}$  (mm.) $^{1/2}$  min. $^{-1}$ ; abscissa,  $(HI)/(I_2)^{1/2}$  (mm.) $^{1/2}$ .

initial slope, showing a small induction period, probably for the build-up of the stationary state for RI. This stationary state concentration for  $i-C_3H_7I$  is very small,<sup>19</sup> but not negligible with our precision. The induction period decreases, of course, with increase in temperature<sup>20</sup> and is insignificant with regard to the total time of runs ( $\geq 13$  hr.). The initial small sigmoid portion of the curve was thus not used for measuring the slopes.

From the plot of  $Z$  vs.  $(HI)/(I_2)^{1/2}$  of expression 3, the intercept,  $I_n$ , was found and was then substituted in conjunction with an assumed value for the inhibition constant,<sup>21</sup>  $k_2/k_3 = 1/5$ , to evaluate the third term. Setting  $\alpha = (1/k_1 K_{I_2}^{1/2})(k_2/k_3)(HI)/(I_2)$ , in eq. 2, a plot of  $(Z - \alpha)$  vs.  $(HI)/(I_2)^{1/2}$  gave, indeed, as expected a linear relation. The intercept and the slope so obtained were used to calculate the rate constants  $k_6$  given in Table I.<sup>22</sup> Figure 2 gives a typical plot of  $(Z - \alpha)$  vs.  $(HI)/(I_2)^{1/2}$  for the same run 39 as for Fig. 1. For run no. 30 and higher series, the over-all equilibrium constant  $K$  was calculated from the values of  $\Delta H^\circ$  and  $\Delta S^\circ$  obtained experimentally from the previous study.<sup>14</sup>  $K_{I_2}$  is calculated from thermodynamic data given in Table II.

(19) The stationary state concentration of  $i-C_3H_7I$  from the above scheme is

$$(C_3H_7I)_{ss} = \frac{K_{I_2}^{1/2}(k_1/k_3)(C_3H_8)(I_2)^{1/2} + (C_3H_8)(HI)\Phi}{K_{5,6} \left[ \Phi + \frac{k_1}{k_6} \frac{K_{I_2}^{1/2}}{K} \frac{(HI)}{(I_2)^{1/2}} \right]}$$

where, as before,  $\Phi = 1 + [k_2(HI)/k_3(I_2)]$ . Under conditions where as much as 1 mm. of  $I_2$  is depleted,  $k_1/k_3$  (600°K.)  $\approx 10^{2.6}$ ,  $K_{I_2}^{1/2} \approx 10^{-2.10}$  (mm.) $^{1/2}$ ,  $\Phi = 1.02 \sim 1.05$  and the second term of the numerator is 2 to 4% of the first term; the sum of three terms in brackets in the denominator is ca. 1.07  $\sim 1.2$ , so that neglecting these,  $(C_3H_7I)_{ss} \approx (k_1/k_3)K_{I_2}^{1/2}(C_3H_8)(I_2)^{1/2}$ . Substituting  $k_1 \approx 10^{11} \times 10^{-25.0/\theta}$  (l./mole sec.), found subsequently, and the known value,  $k_3 \approx 10^{13} \times 10^{-43.0/\theta}$  sec. $^{-1}$ ,  $K_{I_2}^{1/2} = 10^{4.17} \times 10^{-11.0/\theta}$  (converting  $k_1$  into units mm. $^{-1}$  sec. $^{-1}$ ), and  $(I_2)^{1/2}$  about 2  $\sim 4$  (mm.) $^{1/2}$ , we find that  $(C_3H_7I)_{ss} \leq 10^{-2}(C_3H_8) \approx 0.2 \sim 0.4$  mm. on the average, which applies, neglecting the first two points on the  $(I_2)$  vs.  $t$  curve, after zero time.

(20) This observation is in contrast to the case of isobutane (ref. 7) where no induction period is observed and may be due to a higher energy requirement for step 5 in the present case.

(21) The kinetic study of the system  $i-PrI + HI$  in our laboratories suggested this value (unpublished work). Any temperature dependence was neglected.

(22) The intercepts obtained from the two different plots never differed by more than 5–10%. This is due to the circumstance that in the first plots of  $Z$  vs.  $(HI)/(I_2)^{1/2}$ , the measured slopes may be  $\pm 5\%$  from true values, which arises from the practical limitations of drawing smooth curves close to the true curve. However, in the second plot, the linear relation obtaining permits an easy choice with proper emphasis of all the points obtained experimentally.

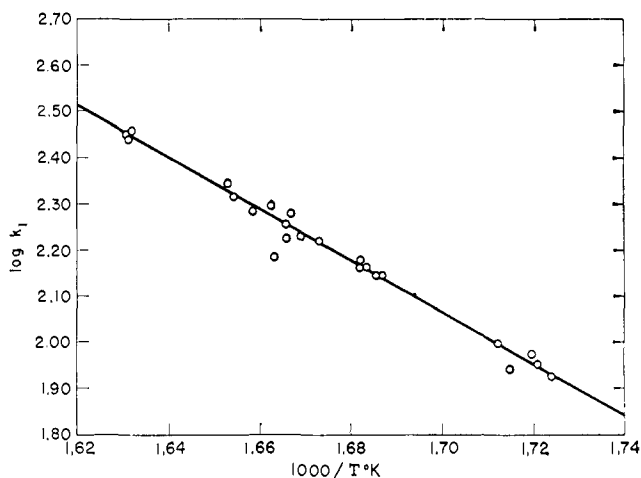


Fig. 3.—Arrhenius plot of  $k_1$ : ordinate,  $\log k_1$ , l./mole sec.; abscissa,  $1000/T$ ,  $^{\circ}\text{K}$ .

The Arrhenius plot of the rate constant  $k_1$ , shown in Fig. 3, is very well described by the equation

$$\log k_1 \text{ (l./mole sec.)} = 11.53 \pm 0.36 - (25.5 \pm 1)/\theta \quad (4)$$

where  $\theta = 2.303RT$  in kcal./mole. The uncertainty of 1 kcal./mole in the activation energy represents the most pessimistic estimate of the scatter in the Arrhenius plot.

TABLE II  
THERMODYNAMIC DATA<sup>a</sup>

Species	$\Delta H_f^{\circ}$ , kal./mole	$C_p^{\circ}$ , cal./mole $^{\circ}\text{K}$ .	$S^{\circ}$ , cal./mole $^{\circ}\text{K}$ .
I <sub>2</sub>	14.9	8.8	62.3
I	25.5	5.0	43.2
HI	6.2	7.0	49.3
H	52.1	5.0	27.4
C <sub>3</sub> H <sub>8</sub>	-24.82	17.57 <sup>b</sup>	64.5
C <sub>3</sub> H <sub>6</sub>	4.88	15.27 <sup>b</sup>	63.80
C <sub>3</sub> H <sub>7</sub> I	-9.46 <sup>c</sup>	21.7 <sup>d</sup>	79.0 <sup>c</sup>

<sup>a</sup> All values are taken from N.B.S. Circular No. 500 (1952), A.P.I. compilation, Project No. 44 (1953), and JANAF Thermochemical Data, D. R. Stull, Ed., Dow Chemical Co., Midland Mich., 1961-1963, unless specified to the contrary. Standard states are ideal gases at 1 atm., 25°. <sup>b</sup>  $C_p^{\circ}$  as function of temperature is found from relations given by H. M. Spencer, *Ind. Eng. Chem.*, **40**, 2152 (1948). <sup>c</sup> Calculated by S. W. Benson and A. Amano, *J. Chem. Phys.*, **36**, 3464 (1962). <sup>d</sup> The value 20.7 cal./mole  $^{\circ}\text{K}$ . calcd. as in preceding note (c), has been corrected by H. Teranishi and S. W. Benson, *J. Chem. Phys.*, in press, from spectroscopic measurements on *i*-PrCl.

We have tacitly assumed that it is the secondary H atom in C<sub>3</sub>H<sub>8</sub> which is responsible for the dehydrogenation process. However, there is no reason to exclude some contribution from the primary H atoms. It is possible to make a reasonable estimate for this latter contribution<sup>28</sup> which we find to be of the order of 15% or less. From this we find that the rate constant for

(23) On the assumption that  $D(\text{C-H})_{\text{primary}} = 98$  kcal./mole as in ethane while  $D(\text{C-H})_{\text{secondary}}$  (as is found subsequently) = 94.5 kcal./mole, the two (C-H) bonds differ by 3.5 kcal. Statistically, the  $A$ -factor for abstraction of primary H atom may be higher than that of secondary H atom by a factor of three, for there are six primary H atoms available compared to two secondary H atoms. If  $k_1^{\text{p}}$  and  $k_1^{\text{s}}$  denote rate constants for abstraction of secondary and primary H atoms, respectively, the relation  $k_1^{\text{p}} = k_1^{\text{s}} + k_1^{\text{p}}$  holds where  $k_1^{\text{p}} = k_1$  (obsd.) given by (4) in the text. Further, at  $T = 600^{\circ}\text{K}$ ,  $x = k_1^{\text{p}}/k_1^{\text{s}} \approx 3 \times 10^{-3/2} = 0.15$ . Further,  $E_1^{\text{p}} = E_1^{\text{s}} + [x(1+x)](E_1^{\text{p}} - E_1^{\text{s}}) = E_1^{\text{s}} + 0.5$  so that  $E_1^{\text{p}} \approx 25.0$  kcal./mole and from the same relation it is found  $A_1^{\text{p}} = 10^{11.22}$  l./mole sec.

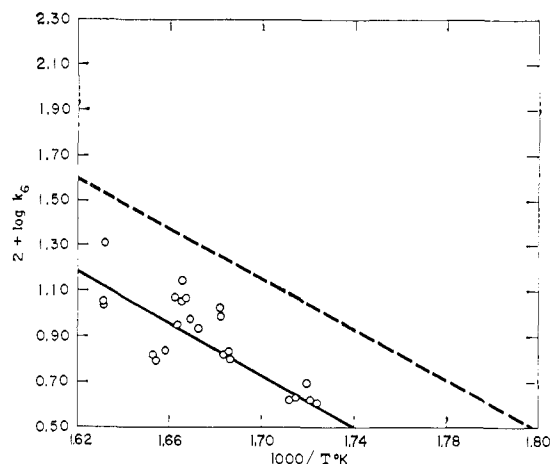


Fig. 4.—Arrhenius plot of  $k_6$ : ordinate,  $2 + \log k_6$ , l./mole sec.; abscissa,  $1000/T$ ,  $^{\circ}\text{K}$ ; dashed line, ---, data of Bose and Benson.

the abstraction of secondary H atoms,  $k_1^{\text{s}}$ , hereafter denoted simply by  $k_1$  has the Arrhenius form<sup>23</sup>

$$\log k_1 = 11.22 - 25.0/\theta \text{ (l./mole sec.)} \quad (5)$$

A similar Arrhenius plot of  $k_6$  shows gross scatter for reasons not now understood (Fig. 4). Despite this scatter, it is possible to derive the parameters given by the equation

$$\log k_6 \text{ (l./mole sec.)} = 7.5 - 23.7/\theta \quad (6)$$

These are in good agreement with the results reported by Bose and Benson,<sup>17</sup> who give

$$\log k_6 = 7.89 - 23.4/\theta \text{ (l./mole sec.)} \quad (7)$$

As can be seen from Fig. 4, our own values for  $k_6$  are consistently smaller than the directly measured values of Benson and Bose by about a factor of 2.5. This should be well outside the estimated errors of both experiments.

If we follow the procedure of Teranishi and Benson and use the known values of  $k_6K$  in eq. 2 to obtain a best fit for  $k_2/k_3$  we find a value for the latter of about 2.0 with relatively large scatter. This is much too large to be reasonable. For about 12 similar systems, values of  $k_2/k_3$  are nearly temperature independent and lie between 0.12 and 0.25. We are forced to conclude that our method for measuring small pressure changes is just not as precise as the spectrophotometric techniques. It should be noted that while the intercepts are relatively insensitive to the choice of values of  $k_6K$  or  $k_2/k_3$ , the slopes can vary greatly and are subject to much larger uncertainties.

The value  $A_1 = 10^{11.22}$  l./mole sec. from (5) is slightly higher than the collision frequency for C<sub>3</sub>H<sub>8</sub> + I. However,  $A$  values  $\geq 10^{11.4}$  (l./mole sec.) have previously been reported for abstraction reactions of I + RI<sup>6b,23</sup> and for I + RH.<sup>7</sup> This seems to be a unique feature of I atom reactions and may be compared with the corresponding reaction of Br atom with C<sub>3</sub>H<sub>8</sub> for which  $A = 10^{10.7}$  (l./mole sec.) has been reported.<sup>12,26</sup> Such high

(24) The production of  $n\text{-C}_3\text{H}_7$  radical by this minor process will of course lead to  $n\text{-C}_3\text{H}_7\text{I}$  production and it can be shown (S. W. Benson, *J. Chem. Phys.*, **38**, 1945 (1963)) that its stationary state concentration will be less than that for *i*-PrI.

(25) S. W. Benson and H. E. O'Neal, *ibid.*, **34**, 514 (1961).

(26) At temperature  $\sim 150^{\circ}$  or lower at which the brominations were carried out, the abstraction of primary H atoms may be shown to be insignificant and the  $A$  factor applies for only secondary H atom abstractions.

A factors can be rationalized in terms of a loose complex in which enhanced entropy of activation arises from low frequency stretching and bending modes involving the I atom.

### Heat of Formation and Bond Strength

The observed value of  $E_1$ , given by (5), may be used to derive the bond dissociation energy,  $D(i\text{-C}_3\text{H}_7\text{-H})$ , if  $E_2$  is known. Flowers and Benson<sup>6b</sup> have reported a value of  $E_2 - E_3 = 0.8 \pm 1.0$  kcal. for the Me radical, Hartley and Benson<sup>10</sup> give  $E_2 - E_3 = 0.9$  kcal. for the  $\text{C}_2\text{H}_5$  radical, and O'Neal and Benson<sup>6a,27</sup> give  $E_2 - E_3 = 1.5$  kcal. for the  $\text{CH}_3\text{CO}$  radical. In the absence of any experimental finding on the isopropyl radical, we may assume it to be between those for Et and  $\text{CH}_3\text{CO}$ , with a chosen value,  $E_2 - E_3 = 1.1$  kcal. If  $E_3 \approx 0.2$  kcal.,<sup>10</sup> then  $E_2 = 1.3$  kcal./mole and we may further deduce  $\Delta H_{1,2}^\circ(600^\circ\text{K.}) = E_1 - E_2 = 23.7$  kcal./mole, at the middle of the temperature range of the present work. From the thermodynamic data given in Table II,  $\Delta C_{p1,2} = 2.1$  cal./mole  $^\circ\text{K.}$ ,<sup>28</sup> which leads to  $\Delta H_{1,2}^\circ(25^\circ) = 23.1$  kcal./mole. Since the bond dissociation energy,  $D^\circ(\text{H-I})_{25^\circ} = 71.4$  kcal./mole,<sup>29</sup> is known very accurately, we can use the relation

$$D^\circ(i\text{-C}_3\text{H}_7\text{-H}) - D^\circ(\text{H-I}) = \Delta H^\circ_{1,2}(25^\circ)$$

(27) H. E. O'Neal and S. W. Benson, *J. Chem. Phys.*, **37**, 540 (1962).

(28)  $C_p^\circ$  for the  $i\text{-C}_3\text{H}_7$  radical is assumed the same as for  $\text{C}_3\text{H}_8$ , and  $C_p^\circ(\text{HI})$  is taken as the mean of the values at  $25^\circ$ ,  $7.0$  cal./mole  $^\circ\text{K.}$ , and at  $600^\circ\text{K.}$ ,  $7.25$  cal./mole  $^\circ\text{K.}$

(29) National Bureau of Standards Circular No. 500, U. S. Govt. Printing Office, Washington, D. C., 1952.

to find

$$D^\circ(i\text{-C}_3\text{H}_7\text{-H}) = 94.5 \text{ kcal./mole}$$

The heat of formation,  $\Delta H_f^\circ(25^\circ)$ , for the  $i\text{-C}_3\text{H}_7$  radical may also be computed from thermodynamic quantities given in Table II from the relation

$$\Delta H_f^\circ(i\text{-C}_3\text{H}_7) = \Delta H_f^\circ(\text{C}_3\text{H}_8) - \Delta H_f^\circ(\text{H}) + D(i\text{-C}_3\text{H}_7\text{-H})$$

and the value obtained is  $\Delta H_f^\circ(i\text{-C}_3\text{H}_7) = 17.6$  kcal./mole with an uncertainty of  $\pm 1$  kcal./mole.

Electron impact measurements<sup>30</sup> have led to  $D(i\text{-C}_3\text{H}_7\text{-H}) = 94 \pm 2$  kcal./mole. From competitive bromination of pairs of alkanes, Fettis, *et al.*,<sup>31</sup> derived the bond dissociation energy,  $D(i\text{-C}_3\text{H}_7\text{-H}) = 93.1$  kcal./mole. In arriving at this value they used the results of Kistiakowsky and van Artsdalen<sup>32</sup> on the bromination of  $\text{CH}_3\text{Br}$  and Polanyi's relation  $E = \alpha\Delta H + C$ . Though the agreement of our data with these values is good, it is difficult to reconcile with the high precision claimed by Fettis, *et al.* It is our own feeling that the scatter in their reported rate constants and the uncertainties associated with both the bromination work and the Polanyi relation introduces an uncertainty of the order of  $\pm 2$  kcal. in their value.

(30) D. P. Stevenson, *Trans. Faraday Soc.*, **49**, 867 (1953).

(31) G. C. Fettis and A. F. Trotman-Dickenson, *J. Chem. Soc.*, 3037 (1961).

(32) G. B. Kistiakowsky and E. R. van Artsdalen, *J. Chem. Phys.*, **12**, 469 (1944).

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## Polarization of Charge-Transfer Bands<sup>1</sup>

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The polarization of the charge-transfer (c.t.) band of  $\pi$ -molecular complexes of tetrachlorophthalic anhydride (TCPA) and aromatic hydrocarbons has been determined by a photoselection method correlating the polarized c.t. absorption with polarized triplet emission of the donor. It is found that the c.t. band is polarized predominantly along the intermolecular axis and perpendicular to the plane of the ring, indicating that a well-defined structure exists even in the excited state, and that the change in the permanent dipole moment, on excitation, is mainly responsible for the intensity of the c.t. band in these complexes. The same technique has been utilized to show that the phosphorescence of quinoline is out-of-plane polarized, hence confirming Dörr and Gropper's assignment of the phosphorescent state of quinoline as a ( $\pi, \pi^*$ ) triplet. This kind of experiment should be utilizable for structure determination of c.t. complexes in solution.

### Introduction

Mulliken<sup>2</sup> has shown that the electric dipole transition moment,  $\mathbf{u}$ , of the charge-transfer transition frequently appearing in molecular complexes with an excited state predominantly described through

$$\psi_e = a^*\psi_{b_1}(\text{D}^+\text{A}^-) - b_1^*\psi_0(\text{D},\text{A}) + \sum d_i^*\psi_{d_i}(\text{D}^*,\text{A}) \quad (a^* \gg b^*, d_i^*) \quad (1a)$$

and a ground state described through

$$\psi_g = a\psi_0(\text{D},\text{A}) + \sum b_i\psi_{b_i}(\text{D}^+\text{A}^-) \quad (a \gg b_i) \quad (1b)$$

is given (in a.u.) by

$$\begin{aligned} \mathbf{u} &= \int \psi_g \mathbf{r} \psi_e d\tau = \int (a\psi_0 + b_1\psi_{b_1} + \sum_{i \neq 1} b_i\psi_{b_i}) \mathbf{r} (a^*\psi_{b_1} - b_1^*\psi_0 + \sum d_i^*\psi_{d_i}) d\tau \\ &\approx a^*b_1 \int (\psi_{b_1} \mathbf{r} \psi_{b_1} - \psi_0 \mathbf{r} \psi_0) d\tau + (aa^* - b_1b_1^*) \int \psi_0 \mathbf{r} \psi_{b_1} d\tau + \sum_{i \neq 1} a^*b_i \int \psi_{b_i} \mathbf{r} \psi_{b_i} d\tau \quad (2) \end{aligned}$$

In the above relations the contributions from ( $\text{D}^+\text{A}^-$ ) have been neglected.<sup>2</sup> The first term in eq. 2 represents the change in permanent dipole moment of the complex on excitation, and was calculated by Mulliken<sup>2</sup> to be of the same order as the transition moments obtained from observed c.t. bands in  $\pi$ -molecular complexes. This moment has a predicted direction along the line joining the centroids of the donating and accepting or-

(1) Supported by a grant from the Air Force Office of Scientific Research.

(2) R. S. Mulliken, *J. Am. Chem. Soc.*, **74**, 811 (1952); *J. chim. phys.*, **61**, 20 (1964).