

ture with the hydrogen on the nitrogen of ring II, structure II of Fig. 7 is proposed for PheH₂620. The spectrum of PheH₂620 is furthermore almost identical with that given by Woodward for a phlorin base³⁴; the proposed structure differs from the phlorin structure

(34) R. B. Woodward, *Ind. Chim. Belge*, **27**, 1293 (1962).

only in that the β -pyrrole positions of ring IV are reduced.

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

The Thermodynamics of the Dehydrogenation of Propane by Iodine Vapor^{1a}

By PRAKASH S. NANGIA AND SIDNEY W. BENSON^{1b}

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In the range 308 to 340° the gas phase reaction, $I_2 + C_3H_8 \rightarrow 2HI + C_3H_6$, proceeds quantitatively to equilibrium with no side reactions. From the measured compositions at equilibrium it is possible to calculate values of K with an estimated precision of $\pm 3\%$ and hence ΔF° with a precision of ± 0.04 kcal. In the short range given, the points fall on an Arrhenius-type plot with $\Delta H^\circ = 27.88 \pm 0.40$ kcal./mole and $\Delta S^\circ = 37.0 \pm 0.69$ gibbs/mole. Using the spectroscopically known and very precise thermodynamic data for I_2 and HI , it is possible to obtain ΔF° , ΔH° , and ΔS° for the reaction, $C_3H_8 \rightleftharpoons C_3H_6 + H_2$. These agree with combinations of data known from independent sources to within 0.02 kcal./mole, 0.12 kcal./mole, and 0.24 gibbs/mole, respectively. This agreement constitutes a very strong support for the assignments of frequencies and internal barriers in C_3H_8 and C_3H_6 .

Introduction

In some recent studies in this laboratory, attention has been focused on the gas phase studies of the iodides. The main reason is that the iodides are well-behaved kinetic systems and consequently lend themselves to a quantitative evaluation of the thermodynamic and kinetic parameters of alkyl radicals and related molecular species. Many studies relating to the reactions of $I_2 +$ olefins and $HI +$ olefins as well as $RI + HI$ have been reported recently from our laboratory.²

From the equilibrium study of reactions of $I_2 +$ olefins, it has been possible to deduce thermodynamic values for variously C–I bonded groups,³ which in turn permits the calculation of thermodynamic properties for various primary, secondary, and tertiary iodides. The products of the pyrolysis reactions of most organic iodides are usually iodine + olefin + alkane.⁴ It was of interest therefore to explore the possibility of reverse processes under suitable conditions of temperature and pressures of reactants. The importance to the equilibrium studies stems from the findings, in this laboratory, of the existence of a discrepancy in thermodynamic quantities, *e.g.*, S° of butene-1, from I atom catalyzed reversible isomerization of butene-1 \rightleftharpoons butene-2.⁵

Two recent publications⁶ from our laboratory have dealt with isobutane as the hydrocarbon. As a natural extension of these studies, the present work describes the equilibrium measurements for the dehydrogenation of propane; the reaction system involved is $C_3H_8 + I_2 \rightleftharpoons C_3H_6 + 2HI$. From the experimentally measured quantities, ΔH° and ΔS° of the above reaction, and precisely known values of ΔH_f° and S° for both I_2 and

HI , the differences in these latter quantities for the dehydrogenation part may be deduced or, *vice versa*, using the values known for all reactants and products, ΔH° and ΔS° of the reaction may be computed and compared with the observed values.

A detailed investigation of the kinetics of the above system has also been carried out with an objective of finding the bond energy of a secondary H atom and will be communicated in due course.

Inasmuch as the reaction system involves a mole change, it can be simply studied by measuring the increase in pressure with time. Most of the work has been carried out by this method while a few runs were made by studying spectrophotometrically the depletion of I_2 with time.

Experimental

Reagents.—C.P. grade propane, supplied by Matheson Co., Inc., was purified by bulb-to-bulb distillations and finally stored in a flask. The small samples taken for reaction purposes were again purified a few times shortly before use. Analysis of these samples by g.l.c. (gas-liquid partition chromatography) on a Perkin-Elmer J-column showed an impurity to the extent of 1% with a retention time corresponding to C_2H_6 . Due corrections were made to determine the actual initial pressures of C_3H_8 throughout the work.

Iodine was of resublimated quality supplied by Allied Chemical Co.

Apparatus.—The apparatus consisted of the standard glass vacuum line, including all stopcocks lubricated with silicone grease. A cylindrical Pyrex glass vessel packed with glass tubes having a volume of *ca.* 900 cc. served as the reaction vessel. Surrounding the reaction vessel, with small air gap in between, was an electrically heated aluminum core furnace which was insulated with glass wool and mounted in a transite box. The temperature of the furnace was controlled to within $\pm 0.2^\circ$ over a period of a few hours by an Electronotherm controller in conjunction with a Wheatstone bridge which had a platinum wire resistance (50 ohms) as one of its arms for sensing the furnace temperature. The temperature of the furnace was determined by using a copper-constantan thermocouple with the fused end fixed deep into a well created in the reaction vessel, a cold junction in ice-water, and a Leeds and Northrup millivolt potentiometer No. 8886. Calibrations of thermocouple against N.B.S. certified metals (zinc, lead, and tin) showed the temperature to be correct to within $\pm 0.2^\circ$ of the absolute value. As the equilibrium runs were kept for a few days, the temperature did change slightly.

(1) (a) This work has been supported by grants from the U. S. Atomic Energy Commission and the National Science Foundation. It is taken in part from the Ph.D. Thesis Dissertation of P. Nangia, 1964. (b) Stanford Research Institute, Menlo Park, Calif., where reprint requests should be sent.

(2) See D. B. Hartley and S. W. Benson, *J. Chem. Phys.*, **39**, 132 (1963), for references to many previous publications.

(3) S. W. Benson and A. Amano, *ibid.*, **36**, 3464 (1962).

(4) S. W. Benson, *ibid.*, **38**, 1945 (1963).

(5) S. W. Benson and A. N. Bose, *J. Am. Chem. Soc.*, **85**, 1385 (1963).

(6) H. Teranishi and S. W. Benson, *ibid.*, **85**, 2887 (1963); **85**, 2890 (1963).

A proper correction was applied to the observed equilibrium pressure, using the ideal gas laws.

The reaction vessel was directly connected to a very sensitive Bourdon spoon gage fitted with a lamp and scale arrangement. The external jacket of the gage and the dead space including the stopcock connecting the reaction vessel to the vacuum line were wound with nichrome wire and heated to temperatures of around 110°. A wooden enclosure surrounding this area, insulated by glass-wool packing, ensured a fairly homogeneous and constant temperature. This also prevented the zero shift of the spoon which occurred due to large fluctuations of the temperature of the jacket around the glass ring seal. The reference side of the spoon gage was always connected to the main vacuum line so as to keep the pressure down to $\sim 10^{-6}$ mm. This also ensured a constant zero pressure on the reference side and eliminated errors in pressure measurements during the runs that might occur due to variation of pressure with temperature if air were used as a buffer. This was almost a necessity in order to have reliability with the high sensitivity obtaining in the present work.

The calibration of the spoon gage was done by using dry air and a wide bore (25 mm. diameter) mercury manometer read to ± 0.01 mm. with the help of a cathetometer. The back of the manometer had diffused light shining on it for accurate measurements. The spoon sensitivity was better than ± 0.016 mm. The scale reading was found to bear a linear relation to the maximum pressure of 100 mm. used for calibration.

The spectrophotometric runs were made with the apparatus described previously.⁶ However, the metal valves used earlier were replaced by glass stopcocks lubricated with silicone grease and heated as before. The metal valves were found to adsorb iodine with time during calibrations. The calibration was carried out by measuring the absorbancy as well as the pressure of iodine introduced in the reaction vessel. The pressures were measured by a spoon gage from 0.5 to 15 mm., with a sensitivity of ± 0.027 mm., by nulling against air whose pressure was read with a silicone oil manometer. The calibration was done at various temperatures and proper values were used for each temperature. A small pressure broadening effect was found at 4800 Å., the maximum absorbancy region. The iodine samples were degassed a few times before being used in each calibration set or in actual experimental runs.

Procedure.—The procedure for starting the run to be followed by pressure measurements was: A small U-trap (~ 5 to 6 mm. diameter) connected on one side to the reaction vessel and to the main line on the other was cooled to temperatures below -10° and a small fresh sample of iodine was sublimed into it, the trap being evacuated continuously. Before introducing iodine, the reaction vessel was cut off by means of the glass tap, so as not to expose it to air once it had been conditioned, by making 3–4 runs which were discarded.⁷ The iodine was degassed by alternate heating and evacuating when cooled to temperatures below -10° . Subsequently, iodine was introduced in the reaction vessel to the desired pressure which did not change for at least 0.5 hr., indicating absence of absorption by grease. This was followed by introducing freshly purified samples of propane after having removed the excess of iodine from the U-trap. The stop watch was started at the instant when about half the desired pressure of propane was reached. The time lag for reading the total pressure from the instant of introducing C_3H_8 was about 5 sec.

All mercury manometers were closed to the vacuum system during the runs and the mercury vapor from the diffusion pump was kept from the reaction system and auxiliary tubes and traps by cooling appropriate traps with Dry Ice.

The time for attainment of equilibrium varied from about 20 to 80 hr. depending on the reaction temperature. The highest temperature used was 613°K. It was found that at a 10° higher temperature (*i.e.*, 623°K.) propane alone showed a pressure increase of about 1–2% over a period of many hours indicating decomposition. It is quite understandable since heterogeneous decomposition in the packed vessel used here could occur. However, no such observation was made at 613°K. or lower temperatures.

The spectrophotometric runs were made at the lowest tempera-

(7) Preliminary experiments made for equilibrium purposes showed that K_p values increased in successive runs until a reproducible value was attained. Our K_p values are based on the pressure increase observed. Traces of oxygen present might oxidize some HI to form H_2O and I_2 with a negative mole change. Further, how H_2O formed may affect the reaction system is not known.

ture ($\sim 310^\circ$) of the range in a similar manner as reported earlier.⁶ In this set of experiments, higher pressures of propane could be used.

At the end of a run the reaction mixture was allowed to pass through a series of U-traps cooled to different temperatures. The first two at -10° or lower (common salt–ice mixture) trapped iodine; the first one (the same as used for introducing iodine) could trap almost the whole of it. These were not cooled at Dry Ice temperatures because olefins were found to react with iodine and HI⁸ in the liquid state. The gaseous mixture passed through a column packed with auramine-O to remove HI before being collected at -196° was presumed to be C_3 compounds and cut off from the traps containing iodine. The whole of the iodine after being brought into the first trap was sublimed into the reaction vessel by heating and the trap was maintained hot until the equilibrium pressure was reached, whereupon the reaction vessel stopcock was closed. The observed pressure due to unreacted iodine was corrected for the temperature and volume of this trap portion ($\sim 1.3\%$ of the reaction system). The sum of this corrected pressure and the increase in pressure observed at the end of a run tallied with the initial I_2 pressure to within $\pm 2\%$. After removing I_2 from the system, it was evacuated for about 20 min. to observe the zero shift of the spoon on the scale, if any. The C_3 compounds were then collected in the small U-trap and expanded into the reaction system. The corrected pressure again agreed with initial pressure of the hydrocarbon within $\pm 2\%$. Finally, this mixture of C_3 compounds was analyzed by g.l.c. on a Perkin–Elmer J-column. The ratio of the areas of propylene to propane agreed very well with the ratio expected from pressure measurements. It thus independently proves the stoichiometry of the reaction, that the amount of iodine consumed is equal to the increase in pressure, and that the amount of olefin formed is equal to the increase in pressure and also to the loss of propane.

Results and Discussion

The results of the equilibrium measurements, over a sufficiently varied initial composition range of the reactants, in the temperature range 581.1–613°K. are summarized in Table I; the subscript "0" denotes ini-

TABLE I
EQUILIBRIUM DATA FOR THE GASEOUS SYSTEM^a

Run	Temp., °K.	$C_3H_8 + I_2 \rightleftharpoons C_3H_6 + 2HI$						K_p (obsd.) ^c
		$(I_2)_e$	$(C_3H_8)_e$	$(I_2)_{eq}$	$(C_3H_8)_{eq}$	$(HI)_{eq}$	$(HI)_{eq}$	
10	612.8	5.66	17.48	1.73	13.55	3.93	7.86	10.35
20	613.0	4.75	24.41	0.97	20.63	3.77	7.55	10.65
21	613.0	8.29	20.39	3.21	15.31	5.08	10.16	10.64
26	603.0	4.75	25.51	1.16	21.92	3.59	7.18	7.25
28	605.0	4.95	26.11	1.18	22.34	3.77	7.54	8.08
29	604.5	7.79	22.87	3.04	18.12	4.75	9.50	7.76
14	593.5	4.83	25.22	1.44	21.83	3.39	6.78	4.94
15	593.8	4.91	25.12	1.46	21.67	3.45	6.90	5.21
16	593.5	4.86	25.70	1.44	22.28	3.42	6.84	4.98
22	581.0	7.30	22.32	3.64	18.66	3.66	7.32	2.95
23	581.3	4.02	28.39	1.17	25.54	2.85	5.70	3.11
24	582.0	7.07	24.06	3.37	20.36	3.70	7.40	2.94
50 ^b	583.1	15.01	224.6	5.36	214.9	9.65	19.30	3.12

^a All pressures and K_p in units of mm. ^b This run was carried out spectrophotometrically. ^c The values of K_p (obsd.) are somewhat different from the values one obtains by using equilibrium pressures given in columns 5–8; *e.g.*, using the data above for run 15 gives $K_p = 5.18$ mm., less by 0.6% than K_p (obsd.). The data for run 22 give the maximum deviation of 2% from the value quoted. These differences arise from the circumstance that in reporting the equilibrium pressures the figures are rounded to second decimal place while K_p (obsd.) values were calculated from direct scale readings and later on changed to mm. units.

tial concentration while "eq" stands for equilibrium quantities. The data when plotted as $\log K_p$ (mm.) *vs.* $1/T$ give a quite good straight line, although the equilibrium data at the lowest temperature are somewhat lower than the fit one obtains from the graph (Fig. 1).

(8) M. H. Back and R. J. Cvetanovic, *Can. J. Chem.*, **41**, 1396, 1406 (1963), have made similar observations.

TABLE II
 THERMODYNAMIC DATA

Temp., °K.	K_p , mm.		ΔF° , kcal.		$2\Delta H_f^\circ(\text{HI})$, kcal.	$\Delta S_p^\circ(\text{I})$, gibbs	$\Delta F^\circ(\text{I})$, kcal.	$\Delta F^\circ(\text{II})$, ^d kcal.	
	Exptl.	Calcd. ^b	Obsd.	Calcd. ^b				Obsd.	Calcd.
583.1	3.19		6.34		-2.82	4.02	-5.16	11.483	11.47
	3.34		6.29						
	3.07		6.39						
	3.12		6.37						
	Av. 3.18		6.35						
Calcd. ^a	3.30	3.258	6.304	6.31					
593.5	4.94		5.94		-2.85	4.00	-5.22	11.144	11.18
	5.16		5.89						
	4.98		5.93						
	Av. 5.03		5.92						
	Calcd. ^a	4.99	4.966	5.92					
603.0	7.25		5.574		-2.86	3.97	-5.25	10.829	10.86
	7.46		5.54						
	7.21		5.58						
	Av. 7.31		5.564						
	Calcd. ^a	7.21	7.194	5.57					
613.0	10.43		5.224		-2.88	3.96	-5.30	10.507	10.54
	10.65		5.208						
	10.64		5.20						
	Av. 10.57		5.20						
	Calcd. ^a	10.66	10.56	5.119					

^a Calculated from eq. 1. ^b Calculated from A.P.I. data and JANAF tables. ^c $\Delta F^\circ(\text{I})$ denotes the standard free energy change for the reaction $\text{H}_2 + \text{I}_2 \rightleftharpoons 2\text{HI}$, and applies similarly to other thermodynamic functions. The subscript "p" in $\Delta S^\circ(\text{I})$ denotes pressure units (in atm.) for the standard state. ^d $\Delta F^\circ(\text{II})$ is the standard free energy change for the dehydrogenation reaction $\text{C}_3\text{H}_8 \rightleftharpoons \text{C}_3\text{H}_6 + \text{H}_2$. Note: $\Delta F^\circ = \Delta F^\circ(\text{I}) + \Delta F^\circ(\text{II})$ where ΔF° stands for the reaction $\text{I}_2 + \text{C}_3\text{H}_8 \rightleftharpoons \text{C}_3\text{H}_6 + 2\text{HI}$.

 TABLE III
 ΔH° , ΔS_p° FOR OVER-ALL REACTION AND DEHYDROGENATION REACTION^a

Temp., °K.	ΔH° , kcal.		ΔS_p° , gibbs		$\Delta H^\circ(\text{II})$, kcal.		$\Delta S_p^\circ(\text{II})$, gibbs	
	Obsd.	Calcd.	Obsd.	Calcd.	Obsd.	Calcd.	Obsd.	Calcd.
583.1	27.88	27.78	37.00	36.76	30.713	30.62	32.98	32.738
593.5	27.88	27.78	37.00	36.77	30.730	30.63	33.00	32.773
603.0	27.88	27.79	37.00	36.78	30.745	30.64	33.03	32.806
613.0	27.88	27.79	37.00	36.79	30.761	30.66	33.04	32.82

^a The observed values of ΔH° and ΔS° are given as in eq. 1; $\Delta H^\circ(\text{II})$ and $\Delta S^\circ(\text{II})$ refer to dehydrogenation reaction as footnote d, Table II. The calculated values are calculated from A.P.I. and JANAF tables.

This plot gives the relation

$$\log K_p (\text{atm.}) = -(27.88 \pm 0.40)/4.575T + 8.09 \pm 0.15 \quad (1)$$

In Table II, column 2a, is given the set of values of K_p (exptl.) corrected to a common temperature and these agree to better than $\pm 3\%$ with the average values

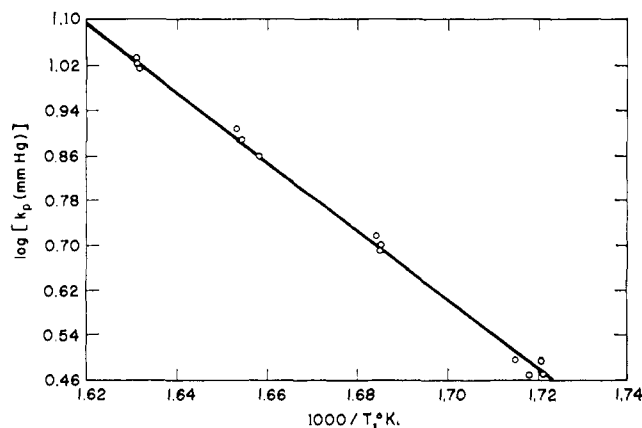


Figure 1.

of K_p also listed in this table. Except at the lowest temperature, the average values of K_p agree with those from eq. 1 within $\pm 2\%$. The available thermodynamic

data for the reaction system⁹ $\text{I}_2 + \text{C}_3\text{H}_8 \rightleftharpoons \text{C}_3\text{H}_6 + 2\text{HI}$ can be used to calculate K_p values and are given in column 2b, Table II, at the four different temperatures. As may be seen, the agreement between the observed and calculated values is extraordinarily good. As noted in the Experimental section, the error in absolute temperature is less than $\pm 0.2^\circ$ and introduces a negligible uncertainty in the measurements. The observed agreement supports the contention that the discrepancies observed⁵ in the butene-1 \rightarrow butene-2 isomerization from those values given in A.P.I. data are real.

Columns 4, 5, and 6 of Table II list thermodynamic quantities for the reaction, $\text{H}_2 + \text{I}_2 \rightleftharpoons 2\text{HI}$. In the first column are given the values for $\Delta F^\circ(\text{II})$, the standard free energy change for the dehydrogenation reaction $\text{C}_3\text{H}_8 \rightleftharpoons \text{C}_3\text{H}_6 + \text{H}_2$, both observed and calculated, and these show almost identical temperature dependence.

In order to observe the temperature dependence of ΔH° and ΔS° , we list in Table III these quantities, calculated from eq. 1 as well as from A.P.I. data and JANAF thermochemical tables. Equation 1 should, as indeed it does, give temperature-independent quan-

(9) See National Bureau of Standards Circular No. 500, U. S. Govt. Printing Office, Washington, D. C., 1952, A.P.I. Compilation (1953), and JANAF Thermochemical Data, D. R. Stull, Ed., Dow Chemical Co., Midland, Mich., 1961-1963. $C_p^\circ(\text{C}_3\text{H}_6)$ and $C_p^\circ(\text{C}_3\text{H}_8)$ are taken from H. M. Spencer, *Ind. Eng. Chem.*, **40**, 2152 (1948).

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 H_2 is known very accurately from statistical mechanical calculations, the difference in S° values for C_3H_6 and C_3H_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 C_3H_8 and C_3H_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° (C_3H_6 - C_3H_8) shows that the magnitudes of these barriers are probably accurate to within 10%.

Kistiakowsky and Nickle¹⁰ 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 I_2 and 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).

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The Kinetics of Dehydrogenation of Propane by Iodine Vapor and the Heat of Formation of the Isopropyl Radical^{1a}

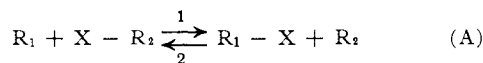
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The kinetics of the gas-phase dehydrogenation reaction $\text{C}_3\text{H}_8 + \text{I}_2 \rightleftharpoons 2\text{HI} + \text{C}_3\text{H}_6$ has been studied manometrically from 308 to 340°. Assuming that the mechanism proceeds by the H atom abstraction, $\text{I} + \text{C}_3\text{H}_8 \xrightleftharpoons[2]{1} \dot{\text{i}}\text{-C}_3\text{H}_7 + \text{HI}$, 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 C_3H_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 ± 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.² The most precise values available today are almost all derived from kinetic studies³ 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 R_1 is a halogen atom and 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 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 CH_4 is based on this assumption.⁵ We have found in our own studies of the reactions of organic radicals with both HI and I_2 that the differences in activation energies between $\text{R} + \text{HI}$ and $\text{R} + \text{I}_2$ are about 1 ± 0.5 kcal.^{6,7} 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 molecules⁶⁻⁸ 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 CH_4 ,^{4,6b,9} C_2H_6 ,^{10,11} and the tertiary C-H bond in isobutane.^{7,12} However, there appear to be no direct measurements of the secondary C-H bond in C_3H_8 and there has been some controversy on its magnitude.¹³

(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.

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(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).