

rate can be determined over a wider range without appreciable error from the diffusional contribution to T_2 .

Acknowledgment. We wish to thank Mr. Fu-ming Chen for his assistance with a number of the calculations.

The Thermochemistry of the Gas Phase Equilibrium

$$\text{I}_2 + \text{C}_3\text{H}_6 \rightleftharpoons \text{C}_3\text{H}_5\text{I} + \text{HI}^1$$

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Contribution from the Stanford Research Institute, Menlo Park, California.
Received March 14, 1966

Abstract: A Cary spectrophotometer, modified for use with high-temperature gas systems, has made it possible to obtain the equilibrium constant for the reaction $\text{C}_3\text{H}_6 + \text{I}_2 \rightleftharpoons \text{C}_3\text{H}_5\text{I} + \text{HI}$ over the temperature range 208–300°. Taking the bond additivity² value $S^\circ_{298}(\text{allyl iodide, g}) = 77.8 \pm 1$ gibbs/mole, the best “third-law” fit to all the temperatures is: $\Delta H_f^\circ_{298}(\text{allyl iodide, g}) = 22.99 \pm 0.6$ kcal/mole (using $\Delta \bar{C}_p^\circ = 1.6 \pm 1$ gibbs/mole). From a Van’t Hoff plot of $\log K$ against $1/T$ (°K), the following thermodynamic quantities were calculated: $\Delta H^\circ_{527} = 8.33 \pm 0.23$ kcal/mole and $\Delta S^\circ_{527} = -1.00 \pm 0.46$ gibbs/mole. When corrected to room temperature, these become $\Delta H^\circ_{298} = 7.96 \pm 0.33$ kcal/mole and $\Delta S^\circ_{298} = -1.91 \pm 0.80$ gibbs/mole. This yields “second-law” values of $\Delta H_f^\circ_{298}(\text{allyl iodide, g}) = 21.46 \pm 0.25$ kcal/mole and $S^\circ_{298}(\text{allyl iodide, g}) = 74.81 \pm 0.80$ gibbs/mole when combined with known values³ for C_3H_6 , HI , and I_2 . The above values of the heat of formation both compare well with a previously measured value⁴ of $\Delta H_f^\circ_{298}(\text{allyl iodide, g}) = 22.0 \pm 3$ kcal/mole and the bond additivity² value of $\Delta H_f^\circ_{298} = 22.7 \pm 3$ kcal/mole, but calculation of the entropy yields agreement with the higher bond additivity figure and supports the third-law values.

By use of a spectrophotometric technique, it has been shown^{5,6} that the kinetic parameters and equilibrium constants of reactions of the type $\text{RH} + \text{I}_2 \rightleftharpoons \text{RI} + \text{HI}$ may be conveniently and accurately determined in the temperature range 200–400°, even though the extent of reaction is small and the equilibria are well to the left. The work presented here concerns the equilibrium constant for the case where R is the allyl radical and thus yields values for the heat of formation and entropy of allyl iodide. The following paper⁷ is concerned with the kinetic parameters and mechanism of the reaction and thus the heat of formation of the allyl radical itself. In order to reduce the rate data meaningfully, it is necessary to know the equilibrium constant data presented here.

Experimental Section

1. Materials. Phillips research grade propylene and reagent grade resublimed iodine were used for the reaction studied. Matheson anhydrous hydrogen iodide and Eastman allyl iodide and isopropyl iodide, all further purified under vacuum, were used for calibration purposes (Dow Corning silicone grease was used on all stopcocks).

2. Apparatus. The apparatus has been described in detail previously.⁵ The spectrophotometric sensitivity toward allyl iodide was found to be such as to permit detection of $\sim 1 \times 10^{-8}$ torr, *i.e.*, 5×10^{-8} mole/l. at the temperatures employed.

3. Procedure. The experiments were performed in a manner essentially analogous to the procedure described previously for the reaction of methane and iodine.⁵ Convenient monitoring wavelengths were 500, 350, 270, 245, and 235 μ , the 350- μ wavelength being used once again as an optical window. The attainment of equilibrium was signified by a lack of change in absorbance after several half-lives. Since the reaction of interest is always followed by the slower reaction of propylene and hydrogen iodide to produce isopropyl iodide, in long duration equilibrium studies it was necessary to make allowances for slight absorption changes due to small concentrations of isopropyl iodide. (Since, as can be seen in the following paper,⁷ the rate of reaction was always followed, it was relatively easy to determine when equilibrium had been attained.)

A further complication arises from the essentially instantaneous formation of small amounts of 1:1 adducts of iodine and propylene over the entire temperature range employed. These adducts turn out to be propylene diiodide and a molecular complex and will be called PI_2 , jointly. They contribute a large absorbance at all the monitoring wavelengths, and this absorbance must be subtracted from the total absorbance in order to determine the absorbance due to allyl iodide and hydrogen iodide. The absorbance due to PI_2 could be determined at any wavelength by observing the initial instantaneous increase in absorbance at that wavelength when propylene was added to the iodine already in the vessel. Plots of this absorbance divided by the product of I_2 and propylene pressures were shown to be linear for several wavelengths and temperatures. The slopes of such plots yield a value for the product of the absorption coefficient and the equilibrium constant for the formation of PI_2 from propylene and iodine.⁸ Thus, the absorbance due to PI_2 can be calculated at any pressure of I_2 and propylene.

(8) At 108° where propylene diiodide is formed slowly, the spectra of the complex and the diiodide were separated. From the known value of the equilibrium constant for the diiodide,⁹ values of the absorption coefficients at various wavelengths could be obtained, assuming these (in concentration units) to be independent of temperature. This permits the calculation of the contribution of the diiodide to the observed PI_2 absorbance. Such a procedure leads to the conclusion that most of the

(1) This investigation was supported in part by a research grant (AP-00353-01) from the Air Pollution Division, Public Health Service, U. S. Department of Health, Education, and Welfare.

(2) S. W. Benson and J. H. Buss, *J. Chem. Phys.*, **29**, 546 (1958).

(3) (a) “Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds,” American Petroleum Institute, Carnegie Press, Pittsburgh, Pa., 1953; (b) “JANAF Interim Thermochemical Tables,” D. R. Stull, Ed., Dow Chemical Co., Midland, Mich., 1963.

(4) O. H. Gellner and H. A. Skinner, *J. Chem. Soc.*, 1145 (1949).

(5) D. M. Golden, R. Walsh, and S. W. Benson, *J. Am. Chem. Soc.*, **87**, 4053 (1965).

(6) R. Walsh, D. M. Golden, and S. W. Benson, *ibid.*, **88**, 650 (1966).

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Table I. Equilibrium Data for the System
 $C_3H_6 + I_2 \rightleftharpoons C_3H_5I + HI^a$

$T, ^\circ K$	Time ^b (min)	$(I_2)_0$	$(C_3H_6)_0$	$(HI)_0$	$(Allyl I)_{eq}$	$(HI)_{eq}$	$(i-PrI)_{eq}$	ΔI_2^c	$K \times 10^4$
482.1	255	19.3	204.5		0.70	0.59	0.11	+0.16	1.09
481.8	213	9.55	459.5		0.695	0.65	0.04	+0.06	1.11
481.8	120	26.5	114.8		0.587	0.587		-0.01	1.16
481.6	240	25.4	420.7		1.14	0.97	0.17	-0.23	1.09
481.4	165	8.05	113.0		0.32	0.305	0.015	+0.06	1.12
515.2	20	10.45	95.4		0.405	0.405		-0.11	1.72
512.9	35	10.2	82.7		0.35	0.35		--	1.50
512.0	34	9.45	128.7		0.427	0.427		--	1.58
512.0	86	9.45	279.2		0.650	0.630	0.02	--	1.67 ^d
512.0	116	9.45	403.3		0.836	0.690	0.146	--	1.67 ^d
512.3	77	26.5	85.0		0.623	0.623		--	1.77 ^d
512.3	187	26.5	452.5		1.48	1.32	0.14	--	1.70 ^d
512.4	30	25.4	464.5		1.48	1.26	0.22	--	1.69
512.5	15	23.8	459.4		1.27	1.27		-0.08	1.57
512.6	24	23.1	105.2	0.59	0.405	0.995		--	1.70
515.0	35	20.4	267.1		0.93	0.93		+0.50(?)	1.66
515.1	17	21.2	449.3		1.19	1.19		-0.19	1.58
514.6	--	10.1	203.2		0.585	0.585		+0.12	1.78
514.7	20	20.3	473.1		1.18	1.18		+0.20	1.56
544.4	10	10.2	108.7		0.594	0.594		-0.15	3.37
544.6	7	23.9	505.8		1.80	1.80		-0.10	2.90
544.6	19	23.9	505.8		1.91	1.84	0.07	--	3.17
544.6	4	11.9	512.2		1.25	1.25		-0.02	2.87
544.7	4	17.2	319.0		1.26	1.26		+0.25	3.15
544.7	5	24.0	61.6		0.756	0.756		+0.10	3.05
544.7	7	4.5	85.8		0.374	0.374		+0.03	3.25
544.4	5	16.1	355.3	1.62	0.645	2.27		-0.01	2.66
571.1	--	4.8	47.4		0.291	0.291		+0.12	4.00 ^d
571.1	--	4.8	362.1		0.76	0.76		--	3.96 ^d
572.7	4	12.5	61.7		0.55	0.55		0.02	4.12
572.6	2	16.6	164.3		1.01	1.01		+0.24	4.00
572.8	3	10.3	178.2		0.84	0.84		-0.01	4.18
572.8	3	12.9	129.3		0.807	0.807		+0.03	4.20
573.0	3	16.65	157.4		1.00	1.00		+0.19	4.10
572.8	3	15.1	143.7	1.8	0.397	2.20		-0.03	4.18
572.7	3	19.8	152.8	2.64	0.373	3.01		+0.20	3.80
572.7	3	18.7	245.8		1.33	1.33		+0.06	4.18

^a All concentrations are pressures in torr at reaction temperature.

^b Times at which absorbances were measured.

^c $(I_2)_f - (I_2)_0 = (Allyl I)_{eq}$

^d These experiments were performed by pressurizing an established equilibrium with propylene.

For calibration purposes HI, *i*-PrI, and allyl iodide were admitted into the vessel individually at various pressures, and their absorption coefficients were determined at 270, 265, and 235 μ for each temperature used. Beer's law was obeyed to better than 3% for absorbances up to 1.8 OD units.

Allyl iodide decomposes at a measurable rate when quantities large enough for calibration purposes are admitted to the vessel; therefore at the higher temperatures it was necessary to extrapolate the observed absorbance *vs.* time curves to zero time. This instability of one of the products of the reaction is not important in the actual experiments since investigations at 240 and 300° showed that the decomposition is severely inhibited by iodine. [In one experiment at 300° 7.7 torr of allyl iodide was admitted to the reaction vessel and the absorbance at 265 μ was monitored until a steady state was obtained ($\sim 10^3$ sec). A scan of the ultraviolet spectrum of products points strongly to the formation of some benzene. The visible spectrum showed that 3.1 torr of I_2 had been formed and the over-all pressure increase was 2.4 torr. If the remainder of the I_2 is converted to 1.5 torr of HI and the hydrocarbon products are propylene, cyclohexane, and benzene, the following concentrations can be calculated from stoichiometry: $C_3H_6 = 3.9$ torr, $C_3H_{10} = 0.55$ torr, and $C_6H_6 = 1.35$ torr.]

The equilibrium I_2 pressure was directly obtainable from the absorbance at 500 μ , the ratio of final to initial absorbance multiplied by the initial pressure yielding the final pressure. The ratio of absorbance at 500 μ was also multiplied by the initial I_2 absorbance at 270, 265, and 235 μ to determine the contributions of I_2 to the final absorbances at these wavelengths.

Equilibrium pressures of allyl iodide and HI were assumed to be equal (except in those runs where HI was added initially, in which case HI produced was assumed equal to allyl iodide) so that to obtain their value the absorbances at the three wavelengths, corrected for I_2 and PI_2 as described above, were divided by the sum of the absorption coefficients of HI and allyl iodide. The average of the resulting three values was used. The average deviations were of the order of $\pm 2\%$. In those cases where the three values were not in agreement, it was found that, whereas the values determined from 235 and 265 μ agreed with each other, the value from 270 μ was high. This is to be expected if *i*-PrI is formed from HI and propylene since this wavelength is close to a maximum in *i*-PrI absorption. The pressure of *i*-PrI could in principle be determined along with that of HI and allyl iodide from the set of three equations in three variables provided by the absorbances at three wavelengths. In fact, P_{i-PrI} was calculated by

absorbance is due to the molecular complex over the range of reaction conditions.

(9) S. W. Benson and A. Amano, *J. Chem. Phys.*, **36**, 3464 (1962).

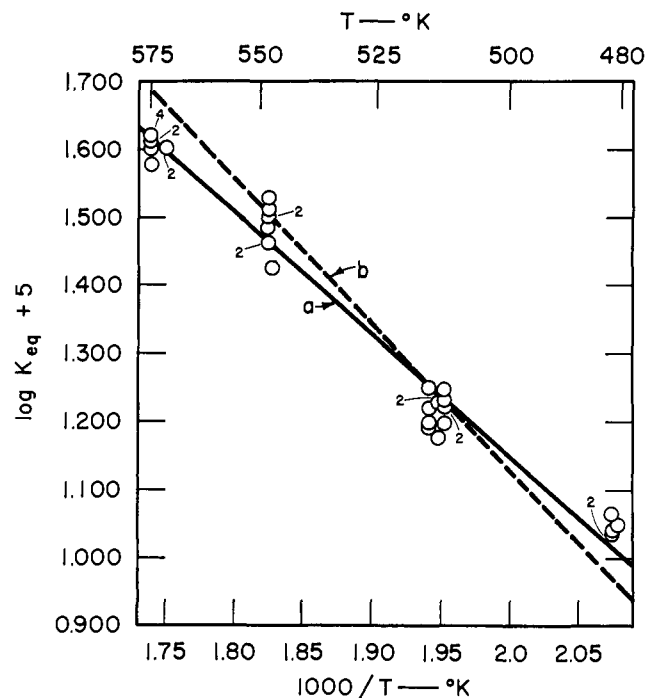


Figure 1. Van't Hoff plot of the equilibrium constant for $CH_2=CH-CH_3 + I_2 \rightleftharpoons CH_2=CH-CH_2I + HI$ (numbers indicate numbers of overlapping points): — (a), curve obtained from least-squares fit; - - - (b), curve obtained from bond additivity entropy.

assuming that $P_{C_3H_5I} = P_{HI} + P_{i-PrI}$ and thus solving two equations in two variables. Such a correction always brought the three wavelengths into agreement.

The final propylene pressure was determined by subtracting the allyl iodide pressure from the initial propylene pressure. Equilibrium constants were determined by dividing the product of final allyl iodide and HI pressures by the product of final I_2 and propylene pressures.

Results

The results of the equilibrium measurements are summarized in Table I and Figure 1. The consistency of the equilibrium constants at each temperature with a 14-fold variation of $(C_3H_6)_0/(I_2)_0$ and the reasonable linearity of the Van't Hoff plot over the 90° range lend credibility to the values obtained.

From the slope and intercept of the solid line in Figure 1 (determined by a computed least-squares fit) values of $\Delta H^\circ_{527} = 8.33 \pm 0.23$ kcal/mole and $\Delta S^\circ_{527} = -1.00 \pm 0.46$ gibbs/mole are determined. $\Delta H^\circ_{298} = 7.96 \pm 0.33$ kcal/mole and $\Delta S^\circ_{298} = -1.91 \pm 0.80$ gibbs/mole are obtained using a value of $\Delta C_p^\circ (= (\Delta C_p^\circ_{527} + \Delta C_p^\circ_{298})/2)$ of 1.6 ± 1 gibbs/mole.¹⁰ Combining these with the well-known values of S°_{298} and $\Delta H_f^\circ_{298}$ for I_2 , HI, and C_3H_6 ,^{3a} leads to "second-law" values of $\Delta H_f^\circ_{298}(\text{allyl iodide, g}) = 21.46 \pm 0.33$ kcal/mole and $S^\circ_{298}(\text{allyl iodide, g}) = 74.81 \pm 0.80$ gibbs/mole. These compare with values of $S^\circ_{298} = 77.8 \pm 1$ gibbs/mole and $\Delta H_f^\circ_{298} = 22.7 \pm 3$ kcal/mole from bond additivity.²

If, on the other hand, the intercept of the Van't Hoff plot is adjusted to agree with the bond additivity en-

(10) Calculation made from equation

$$C_p^\circ(\text{RI}) - C_p^\circ(\text{RH}) = C_p^\circ(\text{CH}_3\text{I}) - C_p^\circ(\text{CH}_2\text{Cl}) + C_p^\circ(\text{C}_2\text{H}_5\text{Cl}) - C_p^\circ(\text{C}_2\text{H}_6)$$

using data at 298, 400, 500, 600, and 700°; see ref 10 of ref 6 for sources of data.

tropy value for allyl iodide, as shown by the dashed line in Figure 1, the "third-law" value for $\Delta H_f^{\circ}_{298}$ becomes 22.99 ± 0.6 kcal/mole. It would, of course, be possible to place the experimental points on the dashed third-law line by varying slightly the magnitude of the corrections applied to take into account the absorbance of PI_2 . Errors quoted in the thermochemical values are from propagation of standard deviations in the Van't Hoff parameters.

Discussion

Gellner and Skinner⁴ give $\Delta H_f^{\circ}_{298}$ (allyl iodide, g) = 22.0 ± 3 kcal/mole, and the value from bond additivity would be 22.7 ± 3 kcal/mole. The reasonably good agreement with both bond additivity and the literature value substantiates the fact the corrections applied were meaningful and reasonable.

Experience seems to show that bond additivity entropies can be trusted to *ca.* ± 1 gibb/mole.^{2,6} Furthermore, it is possible to calculate the entropy of allyl iodide using the spectroscopic assignment of Thompson and Tarkington¹¹ and an assumed twofold barrier to internal rotation of 4 kcal/mole. Such a calculation leads to an entropy of 77.5 gibbs/mole the same as the bond additivity value. To lower the entropy even as much as 1.5 gibbs/mole would mean a barrier of 16 kcal/mole which is certainly too high.

In light of the corrections needed to obtain a second-law plot and the above calculation, it is suggested that the best values are those from bond additivity entropy and the corresponding "third-law" heat of formation.

(11) H. W. Thompson and P. Tarkington, *Trans. Faraday Soc.*, **42**, 432 (1946).

The Kinetics and Mechanism of the Reaction $\text{I}_2 + \text{C}_3\text{H}_6 \rightleftharpoons \text{C}_3\text{H}_5\text{I} + \text{HI}$ and the Heat of Formation of the Allyl Radical¹

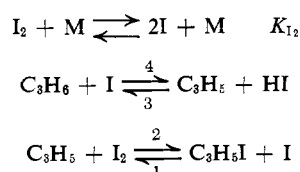
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Received March 14, 1966

Abstract: The reaction of I_2 with C_3H_6 has been followed spectrophotometrically in the gas phase between 208 and 300°. By making use of the equilibrium constant for the system and the usual mechanism for such reactions, a value has been obtained for the rate constant for I-atom abstraction of an allylic hydrogen from propylene, $\log k_4$ (1/mole sec) = $(10.25 \pm 0.14) - (18.04 \pm 0.32)/\theta$. From this activation energy and values for the heats of formation of C_3H_6 , I_2 , and HI, a value of the allylic stabilization energy of 10.2 ± 1.4 kcal/mole is obtained. The difference in stabilization energies of methylallyl and allyl radicals is considered. Differences in A factors for reactions of the type $\text{RH} + \text{I} \rightarrow \text{R} + \text{HI}$ are discussed in terms of the entropy of the transition state.

In the preceding paper² we have discussed the equilibrium measurements for the system $\text{I}_2 + \text{C}_3\text{H}_6 \rightleftharpoons \text{C}_3\text{H}_5\text{I} + \text{HI}$ in the gas phase from 208 to 300°. We have also monitored the approach to equilibrium spectrophotometrically and have found that the data are compatible with the mechanism for reactions of this type elucidated by Benson and O'Neal,³ *viz.*



The activation energy ascertained here for k_4 , taken in conjunction with the generally valid assumption that $E_3 = 1.5 \pm 1$ kcal/mole, leads to a value for $\Delta H_f^{\circ}_{298}$ (allyl, g) and allows evaluation of a stabilization or resonance energy in the allyl radical. The precision of

this work and that of a previous study of the stabilization energy in the methylallyl radical⁴ suggest that the differences in stabilization may be real. Furthermore, there exist enough data on reactions of the type $\text{RH} + \text{I} \rightarrow \text{R} + \text{HI}$ to examine the structural differences of the transition states when R is and is not resonance stabilized.

Some previous values for stabilization energy in allyl radicals have been discussed earlier;⁴ generally they are in the range of 20 kcal/mole.

Experimental Section

Materials, Apparatus, and Procedure. The experiments, materials, and apparatus are described in the preceding paper.² The rate of attainment of equilibrium was followed spectrophotometrically at three different wavelengths using a synchronous motor chart drive.

The value of the rate of HI production, $d(\text{HI})/dt$, at a given time was obtained from the value of the slope of a line drawn tangentially to the absorbance *vs.* time curve at the time in question. Values could also be computed for the allyl iodide and HI concentrations at any time exactly as described in ref 2. The rate constant

(1) This investigation was supported in part by a research grant (AP-00353-01) from the Air Pollution Division, Public Health Service, U. S. Department of Health, Education, and Welfare.

(2) A. S. Rodgers, D. M. Golden, and S. W. Benson, *J. Am. Chem. Soc.*, **88**, 3194 (1966).

(3) S. W. Benson and H. E. O'Neal, *J. Chem. Phys.*, **34**, 514 (1961).

(4) K. W. Egger, D. M. Golden, and S. W. Benson, *J. Am. Chem. Soc.*, **86**, 5420 (1964).