tropy value for allyl iodide, as shown by the dashed line in Figure 1, the "third-law" value for $\Delta H_f°_{298}$ 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 Skinner[4] give $\Delta H_f°_{298}$(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 Tarkington[11] 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 $I_2 + C_3H_6 \rightleftarrows C_3H_5I + HI$ and the Heat of Formation of the Allyl Radical[1]

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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 ± 0.14) − (18.04 ± 0.32)/θ. 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 RH + I → R + HI are discussed in terms of the entropy of the transition state.

In the preceding paper[2] we have discussed the equilibrium measurements for the system $I_2 + C_3H_6 \rightleftarrows C_3H_5I + HI$ 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.*

$$I_2 + M \rightleftarrows 2I + M \qquad K_{I_2}$$

$$C_3H_6 + I \underset{3}{\overset{4}{\rightleftarrows}} C_3H_5 + HI$$

$$C_3H_5 + I_2 \underset{1}{\overset{2}{\rightleftarrows}} C_3H_5I + I$$

The activation energy ascertained here for k_4, taken in conjunction with the generally valid assumption that E_3 = 1.5 ± 1 kcal/mole, leads to a value for $\Delta H_f°_{298}$ (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 radical[4] suggest that the differences in stabilization may be real. Furthermore, there exist enough data on reactions of the type RH + I → R + 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(HI)/d*t*, 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

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(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).

k_4 could then be calculated from the expression

$$k_4 = \frac{d(HI)}{dt}[K_{I_2}^{1/2}(I_2)^{1/2}(C_3H_6)(1 - \alpha)]^{-1}$$

where

$$\alpha = \frac{(C_3H_5I)(HI)}{(C_3H_6)(I_2)}\left(\frac{1}{K_{eq}}\right) \approx \frac{(C_3H_5I)(HI)}{(C_3H_5I)_{eq}(HI)_{eq}}$$

Results

The rate data are presented in Table I. The average deviation from the mean at any temperature never exceeds 10% despite a 14-fold variation of $(C_3H_6)_0/(I_2)_0$ and the fact that rates were taken at various stages of reaction.

Table I. Kinetic Data for the Reaction

$$CH_2 = CHCH_3 + I \xrightarrow{k_4} CH_2 = CH - CH_2 + HI^a$$

$$k_4 = \frac{\partial(HI)}{\partial t}[K_{I_2}^{1/2}(I_2)^{1/2}(C_3H_6)(1 - a)]^{-1}$$

T(°K)	$\frac{\partial(HI)}{\partial t}$ (torr/sec)	a^b	$(I_2)_0$	$(C_3H_6)_0$	$(HI)_0$	(Allyl I)$_t$	$K_{I_2}^{1/2}$ (torr$^{1/2}$)	k_4 (torr^{-1} sec^{-1})
482.1	3.38×10^{-4}	0.01	19.3	204.5		0.077	7.65×10^{-5}	4.96×10^{-3}
481.8	4.45	0.02	9.55	459.5		0.11		4.22
481.8	1.99	0.04	26.5	114.8		0.088		4.54
481.6	6.66	0.05	25.4	420.7		0.23		4.32
481.4	1.11	0.03	8.05	113.0		0.044		4.75
512.0	1.04×10^{-3}	0.02	9.48	128.7		0.061	2.37×10^{-4}	11.3×10^{-3}
512.3	1.15	0.01	26.7	85.0		0.068		11.0
512.5	6.08	0.02	25.5	464.5		0.20		11.2
512.5	5.65	0.02	23.8	459.4		0.20		11.0
512.6	1.03	0.16	23.1	105.2	0.59	0.08		10.4
515.0	3.44×10^{-3}	0.04	20.4	267.1		0.185	2.61×10^{-4}	11.4×10^{-3}
	2.72	0.19				0.41		10.7
515.1	6.2	0.02	21.2	449.3		0.195		11.8
	4.12	0.31				0.70		11.3
514.6	1.67	0.07	10.1	203.2		0.15		10.7
	1.05	0.37				0.36		10.1
514.7	6.46	0.03	20.3	473.1		0.20		12.0
	4.81	0.26				0.64		11.9
	1.35	0.78				1.08		10.8
544.4	7.71×10^{-3}	0.02	10.2	108.7		0.091	6.96×10^{-4}	32.2×10^{-3}
	3.81	0.52				0.415		33.2
544.6	51.4	0.02	23.9	505.8		0.30		30.7
	32.7	0.30				1.04		27.6
544.6	41.9	0.01	11.9	512.2		0.12		34.3
	31.7	0.17				0.56		33.3
544.7	28.5	0.01	17.2	319.0		0.15		31.3
	21.5	0.17				0.54		28.6
544.7	7.85	0.05	24.0	81.6		0.19		29.8
544.7	3.80	0.02	4.50	85.8		0.05		30.6
	2.56	0.39				0.21		33.3
544.4	20.8	0.29	16.1	355.3	1.62	0.27		29.8
571.1	1.02×10^{-2}	0.13	4.8	47.4		0.11	1.41×10^{-3}	80.0×10^{-3}
572.8	3.85	0.27	10.3	178.2		0.45		65.3
572.8	4.66	0.05	12.9	129.3		0.17		74.4
573.0	5.15	0.17	16.7	157.4		0.43		68.8
572.8	2.26	0.63	15.1	143.7	1.8	0.27		77.9
572.7	7.70	0.26	18.7	245.8		0.70		68.8

[a] All concentrations are pressures in torr at reaction temperature.

[b] $a = (\text{Allyl I})(HI)K_{eq}^{-1}(I_2)^{-1}(C_3H_6)^{-1}$; $a^{1/2}$ is the extent of reaction.

Two runs at the lowest temperature performed in a vessel with a 14-fold increase in surface-to-volume ratio showed no increase in rate constant. In one instance the rate constant was evaluated from the integrated form of the rate equation, yielding excellent agreement with the above calculation to 96% of reaction.

The Arrhenius plot of the rate constant in units of torr^{-1} sec^{-1} is shown in Figure 1. The line is a computed least-squares fit which yields the following parameters when converted to concentration units at the mean temperature of 527°K: log A_4 (1/mole sec) = 10.25 ± 0.14; E_4 = 18.04 ± 0.32 kcal/mole.

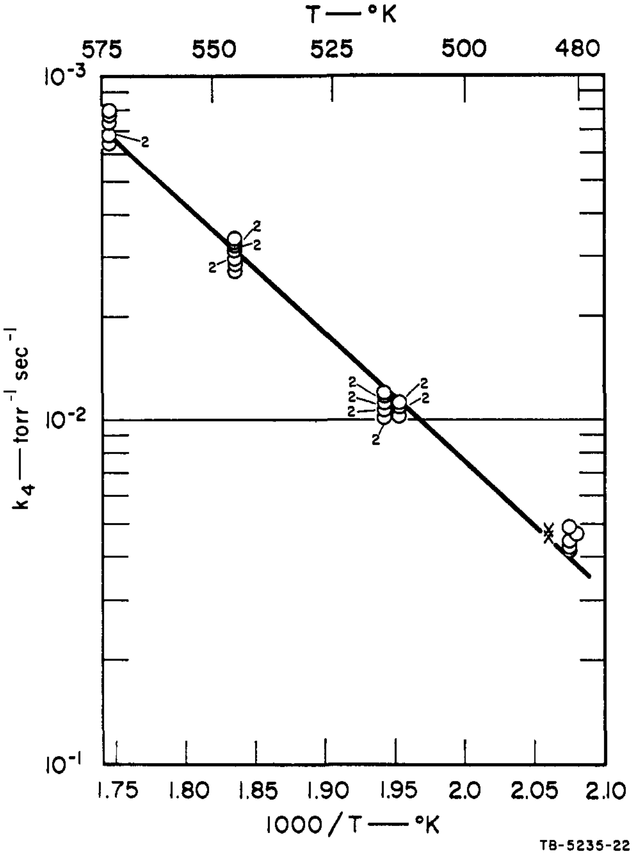

Figure 1. Arrehenius plot for the reaction $CH_2{=}CH{-}CH_3$ + I^- ⟶ $CH_2{=}CH{-}\dot{C}H_2$ + HI (numbers indicate number of overlapping points; X's are runs in a packed vessel).

Using the well borne-out assumption[5] that in this temperature range E_3 = 1.5 ± 1 kcal/mole leads to a value $\Delta H°_{4,3}(527°K)$ = 16.5 ± 1 kcal/mole. The further assumption that $\overline{\Delta C}_{p4,3}$ = 0 ± 2 gibbs/mole means that $\Delta H°_{4,3}(298°K)$ = 16.5 ± 1 kcal/mole. Combining this last value with the known values of the heats of formation of C_3H_6,[6] I, and HI[6] yields $\Delta H_f°_{298}$ (allyl, g) = 40.6 ± 1 kcal/mole. This means that the bond-dissociation energy for the allylic hydrogen in propylene is given by $DH°_{298}(C_3H_5{-}H)$ = 87.8 ± 1 kcal/mole.

The allylic resonance or stabilization energy may be simply defined as the difference between the bond-dissociation energies of a primary hydrogen in propane and the allylic hydrogen in propylene. No good value exists for the former, but it should be very close to the value in ethane which is 98.0 ± 1 kcal/mole. The allylic resonance energy is then 10.2 ± 1.4 kcal/mole. All errors are standard deviations.

Discussion

The difference of 2 kcal/mole between values of the stabilization energy in allyl and methylallyl[4] radicals is barely within the overlap of the error limits of each measurement, but the difference may indeed be meaningful. If the additional methyl group in the methylallyl radical acts to stabilize a partial positive charge on the adjoining carbon atom, in a manner analogous to

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(5) (a) S. W. Benson and H. E. O'Neal, *J. Chem. Phys.*, **34**, 514 (1961); (b) S. W. Benson and P. S. Nangia, *J. Am. Chem. Soc.*, **86**, 2773 (1964); (c) S. W. Benson and H. Teranishi, *ibid.*, **85**, 2890 (1963).

(6) (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.

that discussed by Benson and Haugen[7] in the transition states of four-center addition reactions, the additional stabilization of methylallyl relative to allyl radicals is expected. In the transition state for four-center addition to olefins, the stabilization per methyl group is of the order of ~6–7 kcal/mole, and this does not compare badly with the 2-kcal/mole value reported here considering the differences in charge separation. A possible test is to study the reaction of homologs like 3-methylbutene-1 with I_2 to see if the resonance energy is increased by ~2 kcal/mole due to two methyl groups stabilizing the charge.

In any event, it seems clear that values for allylic and benzylic[8] resonance energies are of the order of 10–12 kcal/mole rather than the higher values obtained by earlier workers discussed elsewhere.[4,8] (Trotman-Dickenson and co-workers[9] have recently shown that high values of allylic resonance energy arrived at by considering the pyrolysis of butene-1 are in error since the measured rate constant is in the fall-off region.) Additional evidence can be obtained from the work of Busfield and co-workers[10] on the decomposition of sulfones. From their values of the rate constant for the decomposition of dimethyl sulfone into CH_3 and CH_3SO_2[10a] radicals and the values for the heat of formation of CH_3 radicals[11] and $CH_3SO_2CH_3$,[10b] the heat of formation of CH_3SO_2 radicals can be obtained on the usual assumption that the recombination reaction has zero activation energy. Thus, from the rate constants for decomposition of $C_3H_5SO_2CH_3$ and $C_6H_5CH_2SO_2CH_3$ and the heats of formation of these compounds, values for the heat of formation of allyl and benzyl radicals of 38 and 47 kcal/mole are obtained. These correspond to stabilization energies of 13 and 14 kcal/mole subject to errors due to differences in temperatures and any error involved in the assumption that the recombination reactions all have zero activation energy.

The value of log A_4 is, as expected, lower than the value for H abstraction by I atoms in normal hydrocarbons due to the stiffening in the transition state resulting from delocalization of the π bond. The value obtained here of log A_4 (l/mole sec) = 10.25 ± 0.14 is higher than that for the same reaction with butene-1.[4] This difference of ~4 gibbs/mole in the entropy of the transition states corresponds to a greater stiffening of the transition state for the abstraction of H from butene-1. This is of the right order of magnitude considering that the delocalization of the π bond causes butene-1 to lose the rotation of a $-C(CH_3)H_2$ group, whereas propylene loses only rotation of a $-CH_3$ group.

Previous experience with the type of reaction reported here allows not only the assumption that $E_3 = 1.5 \pm 1$ kcal/mole, but also indicates that $E_2 = 0 \pm 1$ kcal/mole and $\log A_2/A_3 = 0.5 \pm 0.5$. Thus a value for the entropy of the allyl radical is sufficient for knowledge of all the Arrhenius parameters of reactions 1 through 4. This entropy can be estimated from the entropy of propylene as follows: S°_{500}(allyl) = S°_{500}(propylene) + R ln 2 (electronic degeneracy) − 0.8 (loss of hydrogen deformation) − 3.6 (loss of threefold 2-kcal hindered rotor) + 1.5 (replacement of hindered rotor by ~500 cm^{-1} torsional oscillation) − 1.4 (symmetry) = S°_{500} (propylene) − 2.9 = 73.5 − 2.9 = 70.6 gibbs/mole. This value should not be more uncertain than ±1 gibbs/mole. The values of the four rate constants at 500°K are then (l/mole sec)

$$\log k_1 = (10.3 \pm 0.6) - (6.8 \pm 1)/\theta$$

$$\log k_2 = (9.2 \pm 0.5) - (0 \pm 1)/\theta$$

$$\log k_3 = (8.7 \pm 0.3) - (1.5 \pm 1)/\theta$$

$$\log k_4 = (10.3 \pm 0.1) - (18.0 \pm 0.3)/\theta$$

where $\theta = 2.303RT$ kcal/mole.

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[7] S. W. Benson and G. R. Haugen, *J. Am. Chem. Soc.*, **87**, 4036 (1965).

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

[9] J. A. Kerr, R. Spencer, and A. F. Trotman-Dickenson, *J. Chem. Soc.*, 6652 (1965).

[10] (a) W. K. Busfield and K. V. Ivin, *Trans. Faraday Soc.*, **57**, 1044 (1961); (b) W. K. Busfield, H. Mackle, and P. A. G. O'Hare, *ibid.*, **57**, 1056 (1961).

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