Kinetics and Mechanism of the Gas Phase Reaction between Iodine and Isopropyl Alcohol and the Tertiary Carbon–Hydrogen Bond Strength in Isopropyl Alcohol[1a]

R. Walsh[1b] and S. W. Benson

Contribution from the Department of Thermochemistry and Chemical Kinetics, Stanford Research Institute, Menlo Park, California. *Received March 17, 1966*

Abstract: The gas phase reaction of iodine with isopropyl alcohol has been investigated spectrophotometrically and gas chromatographically within the temperature range 207–300°. The primary products of the reaction were identified as $(CH_3)_2CO$ and HI, while i-C_3H_7I, C_3H_6, C_3H_8, and H_2O were formed by secondary processes. A detailed mechanism is presented in the text. Kinetic measurements over a wide range of initial conditions indicate that the rate-determining step is

$$I\cdot + (CH_3)_2CH(OH) \xrightarrow{4} (CH_3)_2\dot{C}OH + HI$$

with $\log k_4 = 11.07 - (20.5/\theta)$ where $\theta = 2.303RT$ in kcal/mole. When a reasonable value for the back-activation energy is assumed, the bond strength $DH°_{298}((CH_3)_2C(OH)\text{–}H) = 90.3$ kcal/mole is derived. This yields a π-bond energy in acetone of 74.6 ± 1.5 kcal/mole.

Detailed studies of the kinetics and thermochemistry of the gas phase reactions of iodine with a variety of hydrocarbons have proved exceptionally fruitful in providing reliable values for many bond dissociation energies[2] and radical resonance energies,[3] as well as accurate heats of formation of organic iodides.[2a,3b,4] Much of this work has been made possible by the development of a highly sensitive spectrophotometric technique[2–4] which permits detection of as little as 10^{-3} torr pressure of iodine and organic iodides in these systems.

Up to the present, little kinetic work has been done on the reactions of iodine with oxygen-containing compounds. Where molecules of such compounds contain readily abstractable hydrogen atoms, these reactions might reasonably be expected to proceed through the rate-determining step

$$I\cdot + RH \longrightarrow R\cdot + HI$$

as is the case where RH is a hydrocarbon. In this situation, precisely analogous mechanistic considerations would be operative, and a kinetic study should lead to a value for $DH°(R\text{–}H)$. The work presented here represents the first part of more general studies to determine these bond dissociation energies, and is concerned with the case where $R \equiv (CH_3)_2\dot{C}(OH)$. This bond energy, $DH°_{298}((CH_3)_2C(OH)\text{–}H)$, has not previously been measured although Barnard[5] has estimated it to be 90 kcal/mole, a value in essential agreement with calculations of $\Delta H_f°((CH_3)_2\dot{C}(OH),g)$ by Franklin, quoted by Gray and Williams.[6] Its value is important in helping to determine the "π-bond" energy in acetone.

Experimental Section

A. **Materials.** Eastman Kodak isopropyl alcohol (Spectrograde), which was found to be gas chromatographically pure, and research grade resublimed iodine were used. A fresh sample of the alcohol was taken from bottle, dried over calcium chloride, and thoroughly degassed before each run. This was to avoid reaction with or saturation of the grease (silicone) of the stopcocks in the gas-handling system. Eastman acetone (Spectrograde) and Matheson anhydrous hydrogen iodide and isopropyl iodide (the latter purified by several fractional distillations) were used for calibration purposes. Phillips research grade propane and propylene were also used for identification purposes.

B. **Apparatus.** The apparatus was very similar to, though not identical with, one described previously.[2a,3b] As before, it consisted of a quartz reaction vessel placed in an electrically heated furnace (whose temperature was kept constant to ±0.2° in time and ±1.0° in space), and situated above the sample compartment of a Cary Model 15 spectrophotometer. A conventional gas-handling system and Pace pressure transducer were attached.

The only significant difference in design was a change in reaction vessel dimensions, which increased the analyzing light path by a factor of 2, thus doubling the instrument sensitivity for detection of all absorbing species. The limits of detectability were approximately 10^{-3} torr (I_2), 2×10^{-3} torr (HI), and 3×10^{-2} torr (CH_3COCH_3) pressure at 270°.

In addition, an F and M 810 gas chromatograph was used to provide confirmatory analytical evidence for the products. A 15% Hallcomid (6 ft) on DMS treated Chromosorb W was used to separate acetone, isopropyl alcohol, and isopropyl iodide (propylene and propane were also separated from these but not from each other).

C. **Procedure.** Experiments were performed in two stages. The first was designed to obtain detailed information on the product distribution and its variation with time. Spectrophotometric analysis, at both visible and ultraviolet wavelengths, as well as glc analysis were employed for this purpose. The second stage consisted of detailed measurements of initial reaction rates for a variety of initial conditions.

1. **Preliminary Experiments.** Before any run, the reaction vessel was evacuated to 10^{-5} torr and the absorbance of the empty cell was recorded at 500, 350, 280, 260, and 235 mμ. (Since no species in this reaction absorbed at 350 mμ, the base line at 350 mμ served as a convenient reference point when lamps or optical paths were changed.) Iodine was admitted to the reaction vessel to a desired pressure, dried, degassed isopropyl alcohol was added by warming from a liquid reservoir, and an electrical timer (Lab-Chron)

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(1) (a) This investigation was supported in part by Public Health Service Research Grant AP-00353-01 from the Air Pollution Division, Public Health Service; (b) Postdoctoral Research Associate.

(2) (a) D. M. Golden, R. Walsh, and S. W. Benson, *J. Am. Chem. Soc.*, **87**, 4053 (1965); (b) D. B. Hartley and S. W. Benson, *J. Chem. Phys.*, **39**, 132 (1963); (c) P. S. Nangia and S. W. Benson, *J. Am. Chem. Soc.*, **86**, 2773 (1964); (d) M. Teranishi and S. W. Benson, *ibid.*, **85**, 2887 (1963).

(3) (a) K. W. Egger, D. M. Golden, and S. W. Benson, *ibid.*, **86**, 5420 (1964); (b) R. Walsh, D. M. Golden, and S. W. Benson, *ibid.*, **88**, 650 (1966); (c) K. W. Egger and S. W. Benson, *ibid.*, **88**, 241 (1966); (d) A. S. Rodgers, D. M. Golden, and S. W. Benson, *ibid.*, **88**, 3194 (1966).

(4) (a) S. W. Benson and A. Amano, *J. Chem. Phys.*, **36**, 3464 (1962); (b) S. W. Benson and A. Amano, *ibid.*, **37**, 197 (1962); (c) M. Teranishi and S. W. Benson, *ibid.*, **40**, 2946 (1964).

(5) J. A. Barnard, *Trans. Faraday Soc.*, **56**, 72 (1960).

(6) P. Gray and A. Williams, *ibid.*, **55**, 760 (1959).

Table I. Product Distribution[a] in the Gaseous Reaction of I_2 with i-C_3H_7OH

Temp, °K	Residence time, sec	Reactants[b] $[I_2]_0$	Reactants[b] $[i\text{-}C_3H_7OH]_0$	Products[b] [HI]	Products[b] $[(CH_3)_2CO]$	Products[b] $[i\text{-}C_3H_7I]$	Products[b] $[C_3H_6 + C_3H_8]$	Products[b] $[I_2]$	Pressure change,[b] ΔP
511.9	9,400	19.8	28.2	2.72	2.19[c] 2.30[d]	0.79	0.44	18.4	1.7
543.1	14,000	5.93	13.6	3.47	4.3	0.31	...	3.91	4.1

[a] "Product distribution" is used here as a qualitative term, and it is not intended to imply that the product pressures are in fixed ratios during any given run (which is not the case). [b] All pressures in torr. [c] Analysis by glc. [d] Analysis by spectrophotometry.

was started. The total pressure was measured, and the vessel was isolated (the transducer was never left in contact with the reaction mixture because of the danger of material loss, both by absorption and reaction with HI which is known to occur slowly[2a]). During the reaction the absorbances at all wavelengths were periodically measured. After the chosen residence time, the vessel was opened successively to the pressure transducer (to determine final pressure) and a series of U traps, the first two cooled in ice to remove I_2, the next containing solid glycine to remove HI, and the last at −196° to collect the remaining products.

The spectrophotometric base lines were then checked and the contents of the last trap analyzed by gas chromatography. The absorbance time recorded at 280, 260, and 235 mμ were corrected for the contribution of I_2 and converted into product time plots (for HI, CH_3COCH_3, and i-C_3H_7I) by a method involving the solutions of sets of three simultaneous equations. These equations were constructed from calibrations for each absorbing species (note: i-C_3H_7OH did not absorb) and assumed additivity of absorbances. The chromatograph was calibrated for CH_3COCH_3 and total C_3 hydrocarbon. It was not used to analyze for i-C_3H_7I, since unfortunately HI and i-C_3H_7OH reacted to form the iodide in the trapping out system.

2. **Initial Rate Measurements.** Before any run, the reaction vessel was evacuated to 10^{-5} torr. A desired quantity of iodine was then admitted to the reaction vessel and the absorbance at 235 mμ recorded on an expanded recorder sensitivity (×10 scale). The chart drive was then started at a known speed. Dried, degassed isopropyl alcohol was then warmed to a desired total pressure (measured as before). The changing absorbance was recorded automatically until the pen had completely traversed the chart. At this point, the vessel was evacuated, and the products were frozen directly into a trap at −196°. No further analysis was attempted.

From this direct absorbance-time trace and calibrations, initial reaction rates were computed. In the initial stages, these did not reflect precisely the reaction rate due to the finite time required for complete mixing of reactants. However, this time was always short compared with the time for any single run, and an extrapolation to zero time of absorbance differences yielded good approximations to the initial rate of absorbance change. In cases where necessary, a dead space (~4%) correction was applied.

In addition to measurements in a cylindrical quartz reaction vessel (surface-to-volume ratio $\simeq$ 1.0 cm^{-1}) some experiments were performed in a packed vessel (surface-to-volume ratio = 14 cm^{-1}).

Results

A. Preliminary Experiments. The results of two typical experiments are given in Table I. All the observed products are listed, together with the iodine remaining and the pressure change. (On the basis of reasonable agreement of glc and spectrophotometric determinations for acetone, the former method of analysis was discontinued after the first experiment since it was both time-consuming and less accurate.) These results indicate that HI and CH_3COCH_3 are major products while i-C_3H_7I and C_3 hydrocarbon are minor. These facts can be seen much more clearly in Figure 1 which shows the detailed curves of product formation with time as well as the plot of iodine consumption.

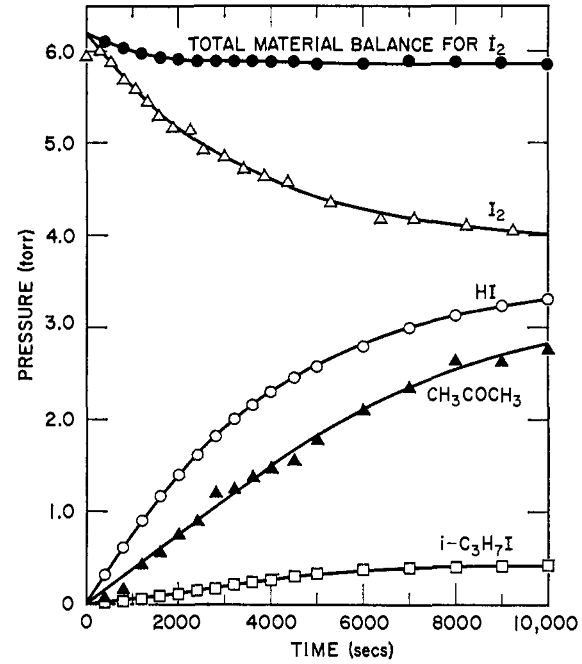

Figure 1. Plot of product formation during the reaction of I_2 (5.93 torr) with i-C_3H_7OH (13.6 torr) at 270°. Slight upward curvature of total I_2 toward zero time results from effect of relaxation of system into dead spaces (4%). Corrections were made to allow for this in rate measurements.

Several features of the reaction are apparent. In the early stages [HI] $\simeq$ $2[CH_3COCH_3]$, and i-C_3H_7I shows all the characteristics of a secondary product which, as the reaction progresses, is formed at the expense of HI. The ratio $[HI]/[CH_3COCH_3]$ steadily decreases from its initial value. The total iodine mass balance can be seen to be good at all times, suggesting that no iodide has been overlooked. C_3H_8 can be accounted for as a product of the reaction of i-C_3H_7I with HI known to occur at these temperatures.[7] C_3H_6 is a product of the simple decomposition of i-C_3H_7I.[4c]

All these facts are embodied in the following over-all reaction scheme

$$I_2 + (CH_3)_2CHOH \xrightarrow{A} 2HI + CH_3COCH_3$$

$$HI + (CH_3)_2CHOH \xrightarrow{B} (CH_3)_2CHI + H_2O$$

$$(CH_3)_2CHI + HI \xrightleftharpoons{C} C_3H_8 + I_2$$

$$(CH_3)_2CHI \xrightarrow{D} CH_3CH{=}CH_2 + HI$$

A represents the principal stoichiometric path, and, since it is a pressure increase reaction, the over-all pressure change should closely reflect acetone formation; Table I shows that this is approximately true. The slight excess of CH_3COCH_3 over ΔP was a persist-

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

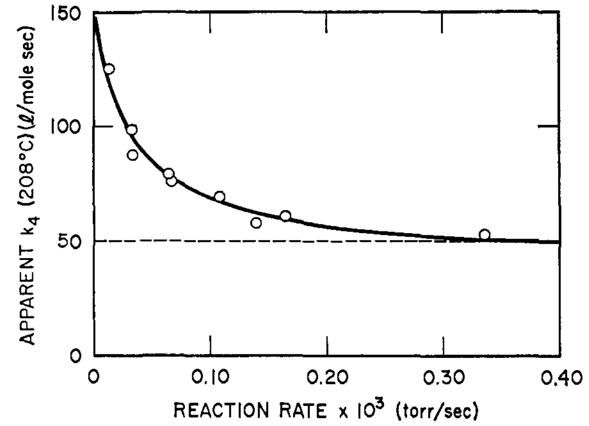

Figure 2. Plot of apparent values of k_4 against over-all reaction rate. Data taken from experiments in unpacked vessel at 208°.

calculations of the rate based on log k_D (sec^{-1}) = 12.96 − (43.5/θ).[4c] The formation curve of i-C_3H_7I appeared to have a zero slope at zero time and showed upward curvature early in the reaction, thus suggesting a reaction such as B to explain i-C_3H_7I formation. That B did indeed occur under these conditions was verified by an independent experiment in which HI and i-C_3H_7OH were mixed and i-C_3H_7I was formed at a steady rate equal to the rate of consumption of HI. No analysis was made for H_2O.

One further characteristic of the reaction, which is suggested by Figure 1, is an approach to steady state of $[I_2]$. The over-all reaction scheme given above will predict such a situation when steps A and C are occurring at equal rates. The implications of this steady state of $[I_2]$ were investigated in more detail, and the results are given after the section on rate measurements.

An additional possible complicating reaction, that of I_2 with CH_3COCH_3, was examined and found to occur negligibly slowly under the conditions of these experiments.

B. Initial Rate Measurements. The results of preliminary experiments suggested that the secondary reactions were not important in the early stages and that the initial rate should reflect only reaction A. These detailed preliminary experiments were carried out at all temperatures (except 300°) at which the subsequent rate measurements were made. Moreover, when rates were measured, the precaution of back extrapolation ensured that true initial rates were obtained. This was important not only to eliminate the possibility of secondary reactions but also because of small but instantaneous rises in absorbance on mixing I_2 with i-C_3H_7OH. These probably resulted from the formation of a weakly bound complex. Such complexes are well known in the liquid phase[8] and have recently been observed in the gas phase.[9]

Initial rate measurements were made in the temperature range 207–300° and interpreted in accordance with the following mechanism which is a simple extension of that established for the reaction of I_2 with hydrocarbons.[7]

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

$$\begin{array}{l}
\mathrm{I}\cdot + (\mathrm{CH_3})_2\mathrm{CHOH} \underset{3}{\overset{4}{\rightleftarrows}} (\mathrm{CH_3})_2\dot{\mathrm{C}}(\mathrm{OH}) + \mathrm{HI} \\
(\mathrm{CH_3})_2\dot{\mathrm{C}}(\mathrm{OH}) + \mathrm{I_2} \underset{1}{\overset{2}{\rightleftarrows}} (\mathrm{CH_3})_2\mathrm{CIOH} + \mathrm{I}\cdot \\
\qquad\qquad\qquad\qquad\qquad\qquad \downarrow 5 \\
\qquad\qquad\qquad\qquad\qquad (\mathrm{CH_3})_2\mathrm{CO} + \mathrm{HI}
\end{array}$$

This mechanism visualizes the formation of an intermediate α-iodohydrin which decomposes rapidly by step 5 (and exists in too low a concentration to be observed). If the further assumption is made that step 3 is slow by comparison with step 2 (this has been verified in *all* iodine reaction systems where $[I_2] >> [HI]$), then step 4 becomes rate controlling and the rate of product formation is given by

$$\left\{\frac{\mathrm{d}[\mathrm{CH_3COCH_3}]}{\mathrm{d}t}\right\}_{t_0} = {}^1/_2\left\{\frac{\mathrm{d}[\mathrm{HI}]}{\mathrm{d}t}\right\}_{t_0} = k_4[\mathrm{I}][i\text{-}\mathrm{C_3H_7OH}] = k_4K_{\mathrm{I_2}}{}^{1/2}[\mathrm{I_2}]^{1/2}[i\text{-}\mathrm{C_3H_7OH}]$$

Thus initial rates should be half-order in iodine and first order in alcohol. k_4 was calculated on this assumption and the resulting values together with other relevant kinetic data are listed in Table II. It can be seen that, except at the lowest temperature and in the packed vessel, the rate constant k_4 was extremely reproducible. With a variation of at least a factor of 400 in the ratio $[i\text{-}C_3H_7OH]/[I_2]$ at 240, 270, and 300°, the validity of the kinetic expression is established over a wide range of initial conditions.

While the apparent values of k_4 are not perfectly reproducible at 208°, they do show a significant trend. This is illustrated clearly in Figure 2 which shows a plot of the observed values of k_4 against over-all reaction rate. The data seem to fit a curve which tends to a constant limiting low value for k_4 at high reaction rates. This result can be readily explained by a rate expression consisting of two terms, the homogeneous rate and an additional term less strongly dependent on reactant concentrations, *viz.*

$${}^1/_2\left\{\frac{\mathrm{d}[\mathrm{HI}]}{\mathrm{d}t}\right\}_{t_0} = k_{\mathrm{v}}[\mathrm{I_2}]^{1/2}[i\text{-}\mathrm{C_3H_7OH}] + k_{\mathrm{s}}[\mathrm{I_2}]^m[i\text{-}\mathrm{C_3H_7OH}]^n$$

When the data were fitted to this equation,[10] the following values for the empirical constants were obtained: $k_v = 1.22 \pm 0.20 \times 10^{-7}$ $\mathrm{torr}^{-1/2}$ sec^{-1}, $k_s = 2.70 \pm 1.70 \times 10^{-6}$ $\mathrm{torr}^{1/2}$ sec^{-1}, $m = 0.17 \pm 0.11$, $n = 0.34 \pm 0.09$. If the constant k_v is identified with $k_4K_{I_2}{}^{1/2}$, then at 207.7°, $k_4 = 4.97 \pm 0.81 \times 10^2$ l./mole sec which is not much less than the lowest apparent value. The finding that the other term contributing to the rate is 0.17 order in iodine and 0.34 in alcohol suggests a concurrent heterogeneous reaction.

In order to test further the validity of the above expression, some rate measurements were made in a packed vessel with a 14-fold larger surface-to-volume ratio. The difficulty of rate measurements was considerably increased, owing to mixing problems and a large rise in the secondary rate of formation of i-C_3H_7I (suggesting that reaction B is also at least partly heterogeneous in nature). However, in these experiments both $[i\text{-}C_3H_7I]$ and [HI] were measured as functions of time, and rates based on total iodide formation were

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[8] See, for example, G. Briegleb, "Electronen-Donator-Acceptor-Komplexe," Springer-Verlag, Berlin, 1961.

[9] (a) F. T. Lang and R. L. Strong, *J. Am. Chem. Soc.*, **87**, 2345 (1965); (b) D. M. Golden, A. S. Rodgers, and S. W. Benson, *ibid.*, **88**, 3196 (1966).

[10] A least-squares fit and error estimates were computed using the Stanford Research Institute regression program.

Table II. Kinetic Data for the Reaction $I\cdot + (CH_3)_2CHOH \longrightarrow (CH_3)_2\dot{C}(OH) + HI$

Temp, °C	$[I_2]_0$, torr	$[i\text{-}C_3H_7OH]_0$, torr	$10^3\left(\frac{d[(CH_3)_2CO]}{dt}\right)_0$, torr/sec	$10^5k_4K_{I_2}^{1/2}$, torr$^{-1/2}$ sec^{-1}	$10^4K_{I_2}^{1/2}$,[a] torr	k_4, l. mole sec
299.0	2.60	22.7	2.70	7.38	15.49	1705
	0.46	66.0	3.27	7.30		1688
	16.5	5.65	1.81	7.89		1823
	1.205	67.3	5.68	7.68		1775
	3.39	9.98	1.351	7.36		1701
	1.685	40.8	4.26	8.05		1860
270.0	1.57	234.3	3.58	1.220	6.55	631
	2.38	188.5	3.60	1.240		641
	17.8	28.2	1.50	1.263		654
	0.433	274.7	2.19	1.211		626
	14.44	5.20	0.244	1.233		638
	5.60	89.2	2.80	1.327		685
238.8	3.17	150.8	0.395	0.147	2.36	200
	1.65	251.6	0.541	0.168		228
	2.75	55.5	0.150	0.163		221
	15.72	6.8	0.0439	0.163		221
	0.58	259.5	0.283	0.143		194
	4.98	45.6	0.166	0.163		221
	19.8	28.2	0.212	0.169		229
237.3	20.3	55.9	0.390	0.155	2.24	221
207.7	3.02	208.6	0.067	0.0185	0.739	75.8
	2.43	87.7	0.0330	0.0242		98.5
	21.74	9.39	0.01374	0.0308		125.3
	10.97	100.2	0.0645	0.0194		79.0
	32.3	111.9	0.1080	0.0170		69.2
	5.96	402.8	0.1391	0.0142		57.7
	21.75	237.7	0.1640	0.0149		60.7
	9.89	49.8	0.0336	0.0215		87.5
	31.6	461	0.335	0.0129		52.5
235.0[b]	20.7	370.8	4.95	0.288	2.04	448
	10.75	159.3	2.46	0.470		731

[a] K_{I_2} is equilibrium constant for $I_2 \rightleftarrows 2I$, calculated from JANAF Tables.[13] [b] Experiments were performed in packed vessel.

calculated. The resulting values of k_4 are shown at the bottom of Table II. Again, they are not reproducible but are higher than corresponding values in the unpacked vessel at temperatures 4° higher. When fitted to a composite rate expression similar to eq 2, with $m = 0.17$ and $n = 0.34$ but with different rate constants k_v', k_s', these latter were calculated to be $k_v' = 1.31 \times 10^{-6}$ torr$^{-1/2}$ sec^{-1} and $k_s' = 2.12 \times 10^{-4}$ torr$^{1/2}$ sec^{-1}. Although the accuracy of these numbers is likely to be limited (probably to ±50%) by the use of only two data points and the assumed order dependence of the surface reaction, they nevertheless appear to be very close to expected. This point is discussed further below.

An Arrhenius plot of k_4 was made and is shown in Figure 3. All values of k_4 from experiments in the unpacked vessel at 240, 270, and 300° were included, together with the two lowest at 208° (which lay within the limits of error of the extrapolated value determined from the composite rate expression). These points were used in a least-squares analysis to determine the line of best fit. The two values of k_4 calculated from k_v and k_v' (determined in unpacked and packed vessels, respectively) are also shown in Figure 3 as triangles, and it can be seen that within error limits they lie on the line of best fit. Thus we feel that, despite the surface effects undoubtedly occurring in this system, our method of correcting for them is sufficiently reliable to guarantee the homogeneity of the rate constant k_4.

Measurements of the slope and intercept of the line of best fit give

$$\log k_4 \text{ (l./mole sec)} = 11.07 \pm 0.09 - \frac{20.47 \pm 0.22}{\theta}$$

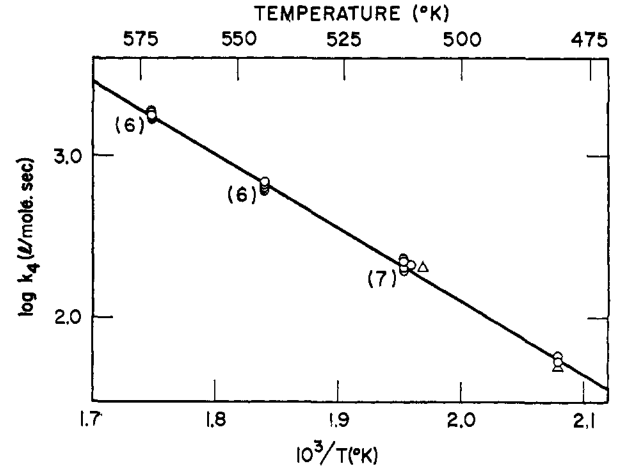

Figure 3. Arrhenius plot for the rate constant k_4. Points used in least-squares estimate of the line marked O; points obtained after correction for surface reaction marked Δ.

If it is assumed that $E_3 = 1.5 \pm 1.0$ kcal/mole,[11] then $\Delta H°_{4,3}(527°K) = 19.0 \pm 1.0$ kcal/mole. It is unlikely that $\Delta\bar{C}_p°_{4,3}$[12] is very far from zero, and if a value of 0 ± 2 cal/mole deg is assumed, then $\Delta H°_{4,3}(298°K) = 19.0 \pm 1.1$ kcal/mole. This value for the heat of reaction ($4 \rightleftarrows 3$) makes possible a calculation of the heat of formation of the radical $(CH_3)_2\dot{C}(OH)$ from the following equation.

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(11) This number with its error brackets all known values for the reaction of radicals with HI. In particular, it is the same as that for $t\text{-}C_4H_9 + HI \longrightarrow i\text{-}C_4H_{10} + I$.[2d]

(12) $\Delta\bar{C}_p°_{4,3} = [\Delta\bar{C}_p°_{4,3}(527°K) + \Delta\bar{C}_p°_{4,3}(298°K)]/2$.

Table III. Steady-State Data in the $I_2 + i\text{-}C_3H_7OH$ Reaction[a]

Temp, °C	Time,[b] min	$[I_2]_0$	$[i\text{-}C_3H_7OH]_0$	$[HI]_{ss}$	$[i\text{-}C_3H_7I]_{ss}$	$[I_2]_{ss}$	$[i\text{-}C_3H_7OH]_{ss}$	$\frac{k_4}{k_9}\frac{1}{K_{eq}}$[c]
27.0	120	2.54	57.1	2.86	0.71	0.76	52.4	0.0511
	110	1.11	30.2	1.39	0.24	0.30	28.9	0.0322
	240	5.93	13.6	3.47	0.31	3.91	7.0	0.0383
	48	1.11	150.3	1.86	0.22	0.059	149.3	0.0463
	50	1.51	234.4	2.88	0.22	0.083	230	0.0328

[a] All pressures in torr; ss ≡ steady state. [b] Time required until $-d[I_2]/dt = 0$. [c] See text for meaning of these constants.

$$\Delta H_f^\circ((CH_3)_2C(OH),g) = \Delta H^\circ_{4,3} - \Delta H_f^\circ(HI,g) + \Delta H_f^\circ((CH_3)_2CHOH,g) + \Delta H_f^\circ(I,g)$$

Substituting known literature values[13] for these heats of formation $\Delta H_f^\circ((CH_3)_2\dot{C}(OH),g) = -27.0 \pm 1.1$ kcal/mole. This value leads directly to $DH^\circ((CH_3)_2C(OH)\text{-}H,g)_{298} = 90.3 \pm 1.1$ kcal/mole.

C. **Steady-State Measurements.** The preliminary experiments indicated that iodine was not totally consumed in this reaction but reached a steady state. This has been explained by the inclusion of the stoichiometric reaction path C. The mechanism for this reaction, a typical HI + organic iodide reaction, is well known.[7]

$$M + I_2 \rightleftarrows 2I\cdot + M$$

$$I\cdot + (CH_3)_2CHI \underset{7}{\overset{6}{\rightleftarrows}} (CH_3)_2\dot{C}H + I_2$$

$$(CH_3)_2\dot{C}H + HI \underset{9}{\overset{8}{\rightleftarrows}} C_3H_8 + I\cdot$$

Neglecting the contributions of steps 1 and 9, a steady-state treatment of steps 2–8 give

$$\frac{-d[I_2]}{dt} = \frac{k_4K_{I_2}^{1/2}[I_2]^{1/2}[i\text{-}C_3H_7OH]}{1 + \frac{k_3[HI]}{k_2[I_2]}} \times \left\{1 - \frac{\left(1 + \frac{k_3[HI]}{k_2[I_2]}\right)}{\left(1 + \frac{k_8[HI]}{k_7[I_2]}\right)} \frac{k_6k_8[i\text{-}C_3H_7I][HI]}{k_7k_4[i\text{-}C_3H_7OH][I_2]}\right\}$$

Thus[14] when $d[I_2]/dt = 0$

$$\frac{[i\text{-}C_3H_7I]_{ss}[HI]_{ss}}{[i\text{-}C_3H_7OH]_{ss}[I_2]_{ss}} \simeq \frac{k_7k_4}{k_6k_8} = \frac{k_4}{k_9}\frac{1}{K_{eq}}$$

where K_{eq} is the equilibrium constant for reaction path C. Thus at steady state for iodine, the concentration ratio on the left-hand side of the above equation should provide a measure of $(k_4/k_9)(1/K_{eq})$.

Several experiments were performed at 270° in an attempt to measure this quantity, and the results are given in Table III. The analyses were quite difficult, which accounts for the rather poor reproducibility. Nevertheless, an order of magnitude value is indicated of $(k_4/k_9)(1/K_{eq}) \simeq 0.04$.

Now this quantity can be checked since k_4 has been measured in the present work, k_9 is known,[2c] and K_{eq} may be estimated from two other known equilibrium constants,[4c,15] *viz.*, those for the systems

$$I_2 + C_3H_8 \rightleftarrows 2HI + C_3H_6{}^{15}$$

and

$$i\text{-}C_3H_7I \rightleftarrows C_3H_6 + HI^{4c,16}$$

Using the following expressions, log k_4 (l./mole sec) = $11.07 - (20.5/\theta)$, log k_9 (l./mole sec) = $11.22 - (25.0/\theta)$, and log $K_{eq} = -0.79 + (7.5/\theta)$, the value of $(k_4/k_9)(1/K_{eq}) \simeq 0.25$ is calculated. The agreement between observed and calculated is poor, and the reasons for this are uncertain. In this temperature range k_4 and k_9 may be regarded as reasonably accurate, but K_{eq} may not be so reliable since the isopropyl iodide decomposition equilibrium constant has never been measured but only calculated from forward and reverse rate constants. Thus we feel that K_{eq} may be unreliable to as much as a factor of 2. However, too much emphasis should not be placed on this because of the suspected surface sensitivity of secondary reactions in the present system, which could affect the observed value for $(k_4/k_9)(1/K_{eq})$.

Discussion

A. **The Mechanism of Reaction A.** The principal aim of this work has been the kinetic study of the primary reaction

$$I_2 + (CH_3)_2CHOH \xrightarrow{A} 2HI + CH_3COCH_3$$

A reasonable mechanism has been suggested in the Results section, and the initial rate of reaction has been shown to be consistent with the kinetics of the slow step 4. In addition, a value of 90.3 kcal/mole has been obtained for the important bond-dissociation energy $DH^\circ((CH_3)_2\dot{C}(OH)\text{-}H)$. This value confirms previous estimates[5,6] and indicates that the bond in question is weaker than the primary C–H bonds (for which strengths of 98 kcal/mole seem reasonable) and the O–H bond (whose strength has been estimated at 102 kcal/mole by Gray and Williams[6]). Thus, because of the selectivity of the iodine atom in hydrogen-abstraction reactions, any contribution to the reaction from any other iodine abstraction path is precluded.

The remaining steps 3, 2, 1, and 5 concern the fate of the $(CH_3)_2\dot{C}(OH)$ radical and the formation and decomposition of the α-iodohydrin. We rejected the possible radical decomposition reaction

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[13] (a) "JANAF Interim Thermochemical Tables," D. R. Stull, Ed., Dow Chemical Co., Midland, Mich., 1963; (b) J. H. S. Green, *Trans. Faraday Soc.*, **59**, 1559 (1963).

[14] $1 + (k_3[HI]/k_2[I_2]) = 1 + (k_3[HI]/k_7[I_2])$, since $k_3/k_2 = k_8/k_7 << 1$; see ref 11.

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

[16] S. W. Benson and G. R. Haugen, *ibid.*, **87**, 4036 (1965).

$$(CH_3)_2\dot{C}(OH) \longrightarrow (CH_3)_2CO + H\cdot$$

(followed by $H\cdot + I_2 \rightarrow HI + I\cdot$) on the grounds that it is 27 kcal/mole endothermic (the activation energy would be even slightly higher) and could not possibly compete with step 2, a reaction expected to have an activation energy ≤ 0.5 kcal/mole (despite the A factors favoring the radical decomposition).

The postulate of the formation of an α-iodohydrin is entirely consistent with the products of systems $I_2 + RH \rightleftarrows RI + HI$ in general,[2-4] and the fact that one is not observed suggests that step 5 in the mechanism is fast. To our knowledge α-iodohydrins have never been prepared. Even if step 5 were not catalyzed either by the surface or in the gas phase, we would expect the four-center elimination of HI to have a very low activation energy in view of the ease of polarization of the transition state for such a path.[16] From an estimate of the maximum value of the pressure of $(CH_3)_2CI(OH)$ which could have existed in the reaction vessel without giving rise to serious inconsistencies in absorbance (provided a reasonable absorption coefficient is assumed), it was calculated that $k_5 \geq 1.38 \times 10^{-2}$ sec^{-1}. A reliable value for the A factor of the four-center elimination reaction is $10^{12.5}$ (by analogy with the decomposition of t-C_4H_9I[17]), so that if k_5 is identified with such a path it may be deduced that $E_5 \leq 34$ kcal/mole. On intuitive grounds we would expect the activation energy to be very much less than that for the t-C_4H_9I decomposition (36.4 kcal/mole), and this result is entirely consistent.

Almost certainly step 1 cannot compete with step 5, and can therefore be disregarded. Furthermore, any over-all back reaction (of HI with CH_3COCH_3) can be rejected on thermodynamic grounds (the equilibrium constant for the reaction predicts almost total conversion to products). For the above reasons, we feel the proposed mechanism is essentially correct and complete.

B. Secondary Reactions. Quantitative data on the reaction of HI with i-C_3H_7OH were not obtained from this work, but from experiments in the packed vessel it appeared to be somewhat surface sensitive. This observation casts some suspicion on the supposedly homogeneous gas phase reactions between alcohols and hydrogen halides studied by Stimson, Maccoll, and co-workers.[18] Reinvestigation of these reactions using HI to catalyze the alcohol decomposition is planned.

C. Some Important Bond Dissociation Energies. A convenient operational definition of the "π-bond" strength in acetone is the reduction in the O–H bond strength in isopropyl alcohol caused by first removing a hydrogen from the α-carbon position, *viz.*, the difference between the heats of the reactions

$$(CH_3)_2CHOH \longrightarrow (CH_3)_2CHO\cdot + H\cdot$$
$$(CH_3)_2\dot{C}OH \longrightarrow (CH_3)_2C{=}O + H\cdot$$

By using Gray and Williams' estimate[6] of 102 kcal/mole for the former reaction, and our own measurements which give 27.4 kcal/mole for the latter, we obtain $D'\pi'(CH_3COCH_3) = 74.6$ kcal/mole. This is probably uncertain to ±1.5 kcal/mole.

It is interesting to note the similarity in the bond strengths $DH°((CH_3)_2C(OH)\text{–}H)$ and $DH°((CH_3)_3C\text{–}H)$[2d] which suggests that the inductive effect of hydroxyl group is the same as that of a methyl group with respect to homolytic bond breaking at the α-carbon position. In addition, the A factors for abstraction of the tertiary hydrogens from isopropyl alcohol and isobutane by iodine atom ($10^{11.07}$ and $10^{10.88}$ l./mole sec,[2d] respectively) are almost identical. If this effect is general, the following bond dissociation energies are indicated: $DH°(CH_2(OH)\text{–}H) = 98$ and $DH°(CH_3CH(OH)\text{–}H) = 94.5$ kcal/mole.

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

(18) V. R. Stimson and E. J. Watson, *J. Chem. Soc.*, 524 (1963), and previous papers referred to therein.