Kinetics of the Reaction of Iodine with Acrolein. Bond Dissociation Energy of the Carbonyl C–H Bond[1a]

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Abstract: The reaction of iodine with acrolein has been studied in the temperature range 172–246°. The initial rates have been found to obey the rate law $-\mathrm{d}(\mathrm{I_2})/\mathrm{d}t = k_3(\mathrm{I})(\text{acrolein})$, and k_3 is given by $\log (k_3/M^{-1}\ \mathrm{sec}^{-1}) = (10.1 \pm 0.2) - (16.8 \pm 0.4)/\theta$. From the activation energy and assuming $E_{-3} = 1 \pm 1$ kcal mol^{-1}, it has been calculated that $D(\mathrm{CH_2CHC(O)}\text{–}\mathrm{H}) = 87.1 \pm 1.0$ kcal mol^{-1}, and $\Delta H_f°(\mathrm{CH_2CH\dot{C}O}, \mathrm{g}) = 17.3 \pm 1.2$ kcal mol^{-1}. The carbonyl C–H bond strength is the same as in formaldehyde reflecting the absence of any stabilization due to the vinyl group. The rate of iodine disappearance decreases with the extent of the reaction according to the scheme $\mathrm{I_2 + CH_2CHCHO \rightleftarrows CH_2CHCOI + HI}$ (3,4) and $\mathrm{CH_2{=}CHCOI \rightleftarrows CH_2{=}C{=}CO + HI}$ (5). k_5 is given by $\log (k_5/\mathrm{sec}^{-1}) = (13.4 \pm 1.0) - (42.8 \pm 7.0)/\theta$.

The C–H bond strength in benzaldehyde, $D(\mathrm{PhC(O)}\text{–}\mathrm{H})$, has been found[2a] to be 86.9 kcal/mol^{-1}, the same as the C–H bond strength in HCHO (87 kcal mol^{-1}),[2b] indicating the absence of any stabilization effect of the phenyl group in contrast to what has been found in the comparison of D(C–H) in ethane (98 kcal mol^{-1})[3] and toluene (85 kcal mol^{-1}).[3] The absence of this 13 kcal mol^{-1} stabilization energy in the case of benzaldehyde has been explained[2a] as due to the fact that in the HCO radical, there is already a "conflicting" stabilization energy of 21 kcal mol^{-1} (by comparison to the *ca.* 108 kcal/mol^{-1} bond strength of $\mathrm{CH_2{=}CH{-}H}$), as a result of conjugation of the odd carbon electron with one of the lone-pair electrons of the O atom. Any interaction with the phenyl ring would be at a cost of the greater stabilization with oxygen and therefore conjugation with the phenyl ring does not occur.

This paper deals with the bond dissociation energy of the carbonyl C–H bond in acrolein and was undertaken in order to see if there is allylic stabilization[4] in the $\mathrm{CH_2{=}CH{-}\dot{C}{=}O}$ radical, or whether, as in the case of benzaldehyde, this stabilization is absent. The bond dissociation energy (BDE) has been studied by the iodination method[5] which has been found to give accurate results for the BDE's of C–H bonds in hydrocarbons and their derivatives.[3,5,6]

Experimental Section

Materials. Acrolein, Baker Reagent, was distilled, and only the middle fraction (about one-half), 52.5°, was collected. This distillate was checked gas chromatographically on a 10-ft column of 20% di-2-ethylhexyl sebacate on 60–80 mesh Chromosorb W and has been found to be at least 99.7% pure. The distillate was kept *in vacuo*, cooled to −35 to −70°, and kept in the dark; yet some polymerization did occur, as indicated by the appearance of a solid white material. The gas phase in the storage vessel was checked for polymerization products, gas chromatographically, and was found to be pure acrolein vapor.

Reagent grade resublimed iodine was obtained from the Mallinckrodt Chemical Co. and was resublimed to a bulb connected to the vacuum system.

Apparatus. The reaction was carried out in a cylindrical quartz vessel, inside a heated thermostated aluminum block, and measured by three thermocouples inside tubes in the reaction vessel. The temperature variation was ±0.1° in time and ±0.4° in space. The absorption of the iodine was monitored with a modified Cary 15 spectrophotometer.[7] The reaction vessel was seasoned (teflonized) by polymerization of 120–180 Torr of $\mathrm{C_2F_4}$ initiated with 1–3 Torr of di-*tert*-butyl peroxide[8] at 170–200°, and the polymerization was quenched by evacuating the remaining gases when the absorption (due to the light scattering by the polymer) of the vessel increased by 0.4–0.6 OD unit. In some of the experiments which have been carried out for long times, some polymerization of the acrolein occurred, as indicated by the increase of the absorption due to scattering. Whenever this extra polymer coating reached the point of increasing the optical density, due to scattering, by 0.15 OD unit, the whole coating was decomposed by heating the vessel to 450° in the presence of air, a procedure which decreases the optical density to the value obtained before coating with Teflon, and a new Teflon coating was formed.

Procedure. Iodine was introduced to the reaction vessel first and its pressure was measured with a Pace differential transducer kept in a hot box at 100–105°. The recorder chart was then started and acrolein was admitted and the total pressure measured. The initial rates of disappearance of iodine were measured after about 2–4 min from the time of admitting the acrolein, in order to allow the mixing of the reactants to be completed. The initial rates were determined by measuring the time required for disappearance of 2–5% of the original iodine.

Results

The rate-determining step for the reaction of iodine with organic compounds has been found, in most cases, to be $\mathrm{I + RH \rightarrow R + HI}$ (a) and/or RHI when RH has a double bond. In both cases, the initial rates will obey the rate law

$$-\mathrm{d}(\mathrm{I_2})/\mathrm{d}t = k_a(\mathrm{RH})(\mathrm{I}) \tag{1a}$$

where (I) and (RH) are the concentrations of the iodine atoms and of the organic compound, respectively. Substituting $(\mathrm{I}) = K_{\mathrm{I_2}}^{1/2}(\mathrm{I_2})^{1/2}$, where $K_{\mathrm{I_2}}$ is the equilibrium

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(6) S. W. Benson, *J. Chem. Educ.*, **42**, 502 (1965).

(7) D. M. Golden, R. Walsh, and S. W. Benson, *J. Amer. Chem. Soc.*, **87**, 4053 (1965); R. Walsh and S. W. Benson, *ibid.*, **88**, 3480 (1966).

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constant for the dissociation of I_2 molecules

$$-d(I_2)/dt = k_aK_{I_2}{}^{1/2}(RH)(I_2)^{1/2} \quad (1b)$$

$$= k_{obsd}(I_2)^{1/2}(RH) \quad (1c)$$

Table I. The Order Dependence of the Initial Rate of Iodine Disappearance (214.5°)

I_2, Torr	Acrolein, Torr	$k_{obsd} \times 10^6$,[a] Torr$^{-1/2}$ sec$^{-1/2}$	$k_a \times 10^{-2}$,[b] l. mol^{-1} sec^{-1}	Run no.
3.4	121	1.21	3.84	1
3.6	44	1.34	4.26	2
5.1	135	1.16	3.68	3
5.8	330	1.34	4.26	4
5.9	43	1.49	4.73	5
11.4	131	1.38	4.38	6
17.2	540	1.24	3.94	7
20.8	696	1.15	3.66	8
23.0	137	1.21	3.84	9

[a] Calculated according to eq 1c. [b] Calculated according to eq 1b. $K_{I_2}{}^{1/2} = 9.52 \times 10^{-5}$ Torr$^{1/2}$ taken from JANAF tables.[9]

Table II. The Temperature Dependence of the Rate Constant

Temp, °C (°K)	I_2, Torr	Acrolein, Torr	$k_{obsd} \times 10^6$,[a] Torr$^{-1/2}$ sec$^{-1/2}$	$1/K_{I_2}{}^{1/2}$	$k_a \times 10^{-1}$,[b] l. mol^{-1} sec^{-1}	Run no.
172.2	2.4	600	4.82		8.29	10
(445.3)	2.9	572	5.13	6.20×10^4	8.85	11
	5.9	542	5.00		8.60	12
172.5	2.0	356	6.25		10.5	13
(445.6)	2.5	390	6.40	6.06×10^4	10.7	14
	3.3	658	4.77		8.00	15
186.7	2.56	583	11.3		10.5	16
(459.8)	3.60	135	17.3		16.0	17
	4.10	480	17.9		16.5	18
	5.15	566	12.6	3.24×10^4	11.6	19
	5.50	254	13.2		12.2	20
	5.60	687	16.9		15.6	21
	17.1	568	11.5		10.6	22
	17.8	637	11.0		10.2	23
199.0	2.90	264	38.6		21.9	24
(472.1)	3.44	581	41.7	1.93×10^4	24.6	25
	5.72	556	32.1		18.3	26
199.4	2.96	593	42.4		23.8	27
(472.5)	4.98	148	45.5	1.905×10^4	25.4	28
	7.45	650	36.8		20.6	29
229.5	8.9	97.5	362		66.8	30
(502.6)	14.2	107	350		64.6	31
	15.1	75	420	5.88×10^3	77.3	32
	15.7	129	364		67.1	33
	18.1	354	348		64.3	34
246.5	9.5	128	1220		128	35
(519.6)	10.5	55	1260		132	36
	12.0	87	1300		136	37
	13.7	59	1010	3.24×10^3	106	38
	14.1	129	1160		122	39
	21.3	162	1180		124	40
	21.4	59.1	1140		120	41
	23.0	102	1090		114	42
175.2[c]	7.3	610	7.25	5.37×10^4	10.9	43
(448.3)	12.7	604	11.3		16.9	44
	19.9	687	10.9		16.3	45
186.3[c]	7.6	526	14.0	3.31×10^4	13.2	46
(459.4)	12.1	412	17.2		16.2	47
	21.5	609	15.4		14.0	48

[a] Calculated according to eq 1c. [b] Calculated according to eq 1b. [c] Experiments done in a packed vessel.

The order dependence of the initial disappearance of iodine, in the reaction with acrolein, was studied at 214.5°. The results are given in Table I, where k_a and k_{obsd} were calculated according to eq 1b and 1c, respectively, using $K_{I_2}{}^{1/2} = 9.52 \times 10^{-5}$ Torr$^{1/2}$.[9] These results show that variations of a factor of 7 in I_2 concentration and 15-fold in the pressure of acrolein give the same rate constant within experimental error, indicating that eq 1a–c also hold for the reaction of iodine with acrolein. These results cannot indicate if the rate-determining step is an abstraction of a hydrogen atom or an addition to the olefin double bond, since both of them will give the same rate law, and this will be discussed later.

The effect of the temperature on the rate constant was measured in the range 172–246° and the results are given in Table II (except those at 214.5°, which have already been given in Table I). These results also show that the dependence on the concentration obeys eq 1, but the variations in the concentration are smaller than in Table I.

Equation 1a gives the time of the measurement, Δt, as

$$\Delta t = \frac{1}{k_{obsd}} \frac{\Delta(I_2)}{(I_2)^{1/2}} \frac{1}{(RH)}$$

For the experiments at high temperatures, for which k_{obsd} is high, in order that Δt will not be too short, we need a large value of $(I_2)^{1/2}/(RH)$, whereas for the low

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[9] D. R. Stull, "JANAF Thermochemical Tables," Dow Chemical Co., Midland, Mich., 1963.

temperatures, this ratio has to be low, such that Δt will not be to long, and the variations in the pressures of the reactants cannot be too extensive.

Least-squares analysis of all the data (Tables I and II) on the temperature dependence, assuming Arrhenius-type dependence, gives

$$\log (k_a/\text{l. mol}^{-1}\,\text{sec}^{-1}) = (10.1 \pm 0.2) - (16.8 \pm 0.4)/\theta$$

where θ is $2.303RT$ kcal mol^{-1}, and the quoted errors are the standard deviations. The plot is shown in Figure 1 (the correlation coefficient is 0.987).

The possibility of a surface catalyzed reaction was checked by using a vessel packed with Pyrex tubes, in which the surface-to-volume ratio was about 14 times larger than in the "normal" vessel. The rate constants measured in the packed vessel are also given in Table II and Figure 1. It seems that at the lowest temperature there may be some surface effect, while at the next highest temperature, this effect is negligible. Also, at the lowest temperature this effect is only about a 60% increase in the rate and, since the surface-to-volume ratio has been increased 14-fold, it seems reasonable that the heterogeneous contribution to the rate constant in the normal vessel is negligible at the lowest temperature.

Discussion

Iodine atoms can react with acrolein by two different routes, both leading to the disappearance of iodine, and both having the same order of dependence: (a) addition to form the diiodo compound (2,3-diiodopropionaldehyde)

$$I + CH_2{=}CH{-}CHO \rightleftarrows CH_2I{-}\dot{C}H{-}CHO \text{ or } \dot{C}H_2{-}CHI{-}CHO \quad (1)$$

$$CH_2I{-}\dot{C}H{-}CHO + I_2 \rightleftarrows CH_2I{-}CHI{-}CHO + I \quad (2)$$

and (b) substitution of a hydrogen atom by an iodine atom to give propenoyl iodide (acrylyl iodide)

$$I + CH_2{=}CH{-}CHO \rightleftarrows CH_2{=}CH{-}\dot{C}O + HI \quad (3)$$

$$CH_2{=}CH{-}\dot{C}O + I_2 \rightleftarrows CH_2{=}CH{-}COI + I \quad (4)$$

It is impossible to know, by measuring the disappearance of iodine, which reaction is taking place. Reaction a occurs mainly at low temperatures, since at high temperature the equilibrium constant for the addition reaction is quite small[10]

$$I_2 + CH_2{=}CH{-}CHO \overset{K_{1,2}}{\rightleftarrows} CH_2I{-}CHI{-}CHO \quad (1,2)$$

The extent of this reaction can be estimated by calculating, from known thermodynamic values, the equilibrium constant, $K_{1,2}$. Since entropy can be predicted quite accurately by bond additivity,[11] the entropy of reaction 1,2 can be estimated to be the same as for the addition of iodine to ethylene or propene, which has been found to be[10] 31.46 cal mol^{-1} deg^{-1}. The heats of formation of acrolein, I_2, and 2,3-diiodopropionaldehyde at 298° are -17.7,[12] 14.9,[14] and -8.2[15] kcal mol^{-1}, respectively. Thus, $\Delta H_{1,2} = -5.4$ kcal mol^{-1} and $\log K_{1,2}$ (atm^{-1}) $= +1180/T - 6.88$. At 445°K, the lowest temperature for which we study the reaction of iodine with acrolein, $K_{1,2}$ is equal to 1.7×10^{-4} atm^{-1} or 2.3×10^{-7} Torr^{-1}. The maximum fraction of iodine that can react by addition to the olefinic double bond is given by 2.3×10^{-7}(Acr), where (Acr) is the pressure of the acrolein in Torr. The maximum pressure of acrolein was 700 Torr; thus the maximum fraction of iodine reacting by addition is 1.6×10^{-4}, while the fraction measured in our experiments was $2\text{-}5 \times 10^{-2}$, which means that the addition of iodine to acrolein can be neglected. At the higher temperatures, $K_{1,2}$ is smaller and hence the fraction of the iodine added to acrolein is even smaller.

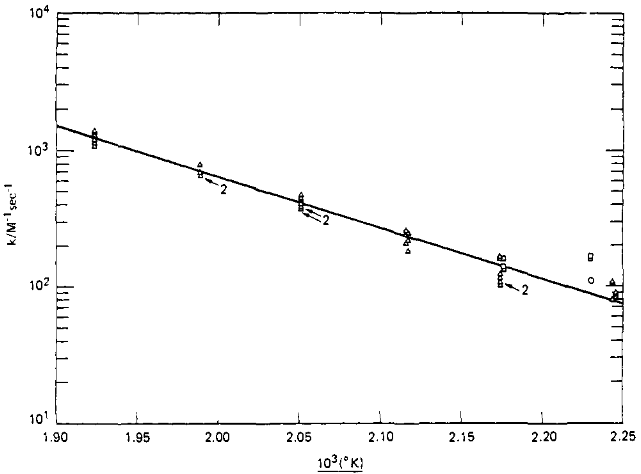

Figure 1. Arrhenius plot for the rate constant of the reaction $CH_2CHCHO + I \rightarrow CH_2CH\dot{C}O + HI$ (3). Numbers indicate number of overlapping points: (△) measurements done in the "normal" vessel; (□) measurements carried out in the packed vessel.

Initial Rates. Since the addition reaction can be neglected, the initial rate constant can be identified as k_3, the rate constant of abstraction of a hydrogen atom by an iodine atom. The A factor for similar reactions with other aldehydes has been found to be $10^{10.9}$ for formaldehyde[2b] and $10^{10.1}$ for benzaldehyde[2a] and a value of $10^{10.3}$ was assumed for the reaction with acetaldehyde.[16] Our value of $10^{10.1\pm0.2}$ is in a good agreement with these results.

Bond Dissociation Energy, $D(CH_2CHC(O){-}H)$. The bond dissociation energy (BDE) can be calculated from the enthalpy of reaction 3, since the enthalpy of the reaction is the difference between the BDE of the broken bond, $D(CH_2CHC(O){-}H)$, and the BDE of the newly formed bond [$D(H{-}I) = 71.3$ kcal mol^{-1}].[17] The activation energy, E_{-1}, for the reaction of a radical with a hydrogen iodide molecule is usually assumed to be 1 ± 1 kcal mol^{-1};[5] hence, ΔH_1 (484°) $= 16.8 - 1.0$

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

[11] S. W. Benson, "Thermochemical Kinetics," Wiley, New York, N. Y., 1968.

[12] The heat of formation can be calculated by group additivity method[13] $CH_2CHCHO{=}Cd(H)_2 + Cd(H)(CO) + CO(Cd)(H) = -17.74$ kcal mol^{-1}. Anderson and Hood, "Acrolein," Wiley, New York, N. Y., 1962, p 27, reported an unpublished result of -17.79 kcal mol^{-1}.

[13] S. W. Benson, *et al.*, *Chem. Rev.*, **69**, 279 (1969).

[14] Reference 11, p 196.

[15] $CH_2ICHICHO$ is given by group additivity as $C(I)(H)_2C + C(H)(I)(C)(CO) + CO(H)(C)$. The first and the last groups are given in ref 13, 7.95 and -29.6 kcal mol^{-1}, respectively. The second group can be calculated from the heat of formation of 2-iodo-3-butanone (-38.2 kcal mol^{-1}: R. K. Solly, D, M. Golden, and S. W. Benson, *Int. J. Chem. Kinet.*, 2, 393 (1970)) and the values of the other groups in this molecule (ref 13) as 13.5 kcal mol^{-1}.

[16] R. Walsh and S. W. Benson, *J. Phys. Chem.*, 70, 3751 (1966).

[17] B. deB. Darwent, "Bond Dissociation Energies in Simple Molecules," NSRDS-NBS Report No. 31, National Bureau of Standards, Washington, D. C., 1970.

$= 15.8 \pm 1.2$ kcal mol^{-1}. To calculate the BDE we have to correct the enthalpy to 298°K. Assuming the heat capacity change $\overline{\Delta C_p}$ to be the same as has been estimated for the reaction of an iodine atom with acetaldehyde,[16] 0.10 cal mol^{-1} deg^{-1}, $\Delta H_1(298°) = 15.8 \pm 1.2$ kcal mol^{-1} and $D(\mathrm{CH_2CHC(O)\text{-}H}) = 87.1 \pm 1.2$ kcal mol^{-1}. From this bond strength and the heats of formation of the acrolein[12] and of the hydrogen atom,[11] the heat of formation of the $\mathrm{CH_2CH\dot{C}O}$ radical is

$$\Delta H_f°(\mathrm{CH_2CH\dot{C}O}, \mathrm{g}) = 17.3 \pm 1.2 \text{ kcal mol}^{-1}$$

The BDE of the carbonyl C–H in acrolein, 87.1 ± 1.2 kcal mol^{-1}, is the same as the carbonyl C–H bond strength in formaldehyde and acetaldehyde (87 ± 1 kcal mol^{-1}),[5] indicating no extra stabilization energy as a result of the allylic group, the same as was found previously for the phenyl group. The fact that the different α substituents (H, $\mathrm{CH_3}$, $\mathrm{C_6H_5}$, $\mathrm{CH_2{=}CH}$) in aldehydes have no effect on the carbonyl C–H bond strength leads to the generalization that the BDE of the carbonyl C–H bond in aldehydes is constant, 87 ± 1 kcal mol^{-1}. This is in contrast to many other C–H bonds where α substituents change the bond strength. The explanation has been discussed in the introduction.

That there is no extra stabilization in the acrylyl radical due to the allylic resonance seems to indicate that the acrylyl radical is a σ radical and not a π radical like the allylic radical, as has been found for the benzoyl radical.[18]

Appendix. Reactions after the Initial Step

The rate of disappearance of iodine decreases with time and this decrease is larger than expected from the $(\mathrm{I_2})^{1/2}$ dependence. This is normal in cases where the equilibrium constant for the formation of the iodide (eq 3,4) is not small enough to be neglected, and the

$$\mathrm{RH} + \mathrm{I_2} \overset{K_{3,4}}{\rightleftarrows} \mathrm{RI} + \mathrm{HI} \qquad (3,4)$$

back reaction inhibits the disappearance of iodine. In this case the rate equation becomes

$$-\frac{\mathrm{d(I_2)}}{\mathrm{d}t} = \frac{k_3(\mathrm{I})(\mathrm{RH})\left[1 - \dfrac{1}{K_{3,4}}\dfrac{(\mathrm{RI})(\mathrm{HI})}{(\mathrm{RH})(\mathrm{I_2})}\right]}{1 + k_{-3}(\mathrm{HI})/k_2(\mathrm{I_2})} \qquad \text{(I)}$$

neglecting $k_{-3}(\mathrm{HI})/k_2(\mathrm{I_2})$ (smaller than 0.1 unless HI is added initially or after more than 50% conversion[5]) and substituting

$$k_3(\mathrm{I})(\mathrm{RH}) = \left(-\frac{\mathrm{d(I_2)}}{\mathrm{d}t}\right)_{t=0}$$

gives

$$K_{3,4} = \frac{(\mathrm{RI})(\mathrm{HI})}{(\mathrm{RH})(\mathrm{I_2})}\bigg/\left[1 - \frac{\mathrm{d(I_2)}}{\mathrm{d}t}\bigg/\left(\frac{\mathrm{d(I_2)}}{\mathrm{d}t}\right)_{t=0}\right] \qquad \text{(II)}$$

Equation II can be applied to our results, assuming (RI) = (HI) = $\Delta(\mathrm{I_2})$. The result of the application of this equation to different stages of one run at 199° is given in Table III. The fact that $K_{3,4}$ is not constant and depends on the extent of the reaction (the same behavior was also found for the other runs) indicates that eq II is not appropriate for this system. The monotonous increase of $K_{3,4}$ with the extent of the reaction suggests that the reason for the failure of eq II is the instability of the iodide which decomposes, most probably by HI elimination, as has been found in the reaction of iodine with methyl ethyl ketone at the higher temperatures.[19] Taking into account the decomposition of the iodide

Table III. Results of Application of Equations II, V, and VII to Run 25[a] at Different Times

$(\mathrm{I_2})$, Torr	$-\frac{\mathrm{d(I_2)}}{\mathrm{d}t}$, Torr sec^{-1}	$\frac{\mathrm{d(I_2)}}{\mathrm{d}t}\Big/\left(\frac{\mathrm{d(I_2)}}{\mathrm{d}t}\right)_{t=0}$	$K_{3,4} \times 10^4$ [b]	$K_{3,5} \times 10^4$,[c] Torr	$k_5K_{3,4} \times 10^7$,[d] sec^{-1}
3.04	3.14×10^{-4}	0.70	3.9	6.08	1.68
2.84	2.605×10^{-4}	0.58	6.15	14.5	1.98
2.56	1.73×10^{-4}	0.382	9.5	33.1	2.16
2.27	9.9×10^{-5}	0.22	14.5	67.2	1.83

[a] 199.0°, $(\mathrm{I_2})_{t=0} = 3.43$ Torr, (acrolein) = 581 Torr, $-(\mathrm{d(I_2)}/\mathrm{d}t)_{t=0} = 4.48 \times 10^{-4}$ Torr sec^{-1}. [b] Calculated according to eq II. [c] Calculated according to eq V. [d] Calculated according to eq VII.

$$\mathrm{CH_2{=}CHCOI} \rightleftarrows \mathrm{CH_2{=}C{=}CO} + \mathrm{HI} \qquad (5)$$

leads to the rate equation[19,20] (assuming steady state for $\mathrm{CH_2{=}CH\dot{C}O}$ and for $\mathrm{CH_2{=}CHCOI}$)

$$-\frac{\mathrm{d(I_2)}}{\mathrm{d}t} = \frac{k_3(\mathrm{I})(\mathrm{RH})\left[1 - \dfrac{1}{K_{3,5}}\dfrac{(\mathrm{olefin})(\mathrm{HI})^2}{(\mathrm{RH})(\mathrm{I_2})}\right]}{1 + \dfrac{k_{-3}(\mathrm{HI})}{k_4(\mathrm{I_2})}\left[1 + \dfrac{k_{-4}}{k_5}(\mathrm{I})\right]} \qquad \text{(III)}$$

where RH and olefin stand for acrolein and $\mathrm{CH_2{=}C{=}CO}$, respectively, and $K_{3,5}$ is the over-all equilibrium constant, $K_{3,5} = k_3k_4k_5/k_{-3}k_{-4}k_{-5}$. Equation III can be simplified[19] for the following cases.

(a) Reaction 5 proceeds at a rate considerably greater than that of reaction 4 (*i.e.*, $k_5 > k_{-4}(\mathrm{I})$); in this case the rate equation will be of the form

$$-\frac{\mathrm{d(I_2)}}{\mathrm{d}t} = \frac{k_3(\mathrm{I})(\mathrm{RH})\left[1 - \dfrac{1}{K_{3,5}}\dfrac{(\mathrm{olefin})(\mathrm{HI})^2}{(\mathrm{RH})(\mathrm{I_2})}\right]}{1 + k_{-3}(\mathrm{HI})/k_4(\mathrm{I_2})} \qquad \text{(IIIa)}$$

(b) The opposite case, $k_5 < k_{-4}(\mathrm{I})$, in which the rate equation becomes[19]

$$-\frac{\mathrm{d(I_2)}}{\mathrm{d}t} = \frac{k_5K_{3,4}(\mathrm{RH})(\mathrm{I_2})}{(\mathrm{HI})}\left[1 - \frac{1}{K_{3,5}}\frac{(\mathrm{olefin})(\mathrm{HI})^2}{(\mathrm{RH})(\mathrm{I_2})}\right] \qquad \text{(IV)}$$

as long as $(k_{-3}(\mathrm{HI})/k_4(\mathrm{I_2}))(k_{-4}(\mathrm{I})/k_5) \gg 1$ (*i.e.*, after about 20–30% of reaction).

We have tried to fit our data to each of these equations. Applying eq IIIa we neglect $k_{-3}(\mathrm{HI})/k_4(\mathrm{I_2})$ and substitute $k_3(\mathrm{I})(\mathrm{RH}) = -(\mathrm{d(I_2)}/\mathrm{d}t)_{t=0}$. Rearranging the equation gives

$$K_{3,5} = \frac{(\mathrm{olefin})(\mathrm{HI})^2}{(\mathrm{RH})(\mathrm{I_2})}\bigg/\left[1 - \frac{\mathrm{d(I_2)}}{\mathrm{d}t}\bigg/\left(\frac{\mathrm{d(I_2)}}{\mathrm{d}t}\right)_{t=0}\right] \qquad \text{(V)}$$

The application of this equation to run 25 is also given in Table III. In these calculations we assume (olefin) = $\Delta(\mathrm{I_2})$ and (HI) = $2\Delta(\mathrm{I_2})$. As is seen from the results in Table III, $K_{3,5}$ is not constant through the reaction and it increases with the extent of the reaction. This would have been clear from comparison of eq II and V

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[18] P. J. Krusic and T. A. Rettig, *J. Amer. Chem. Soc.*, **92**, 722 (1970).

[19] R. K. Solly, D. M. Golden, and S. W. Benson, *Int. J. Chem. Kinet.*, **2**, 381, 393 (1970).

[20] P. S. Nangia and S. W. Benson, *J. Amer. Chem. Soc.*, **86**, 2773 (1964).

without any calculation. Dividing eq V by II gives $K_{3,5} = 4\Delta(I_2)K_{3,4}$ and since both $K_{3,4}$ and $\Delta(I_2)$ increase with the extent of the reaction $K_{3,5}$ will also increase, and at a greater rate than $K_{3,4}$. Thus the conclusion is that eq V does not hold in our case. The next thing is to try to apply eq IV. Rearranging and substituting $k_5K_{3,4}/K_{3,5} = k_{-5}$ gives

$$-\frac{d(I_2)}{dt} = \frac{k_5K_{3,4}(RH)(I_2)}{(HI)} - k_{-5}(\text{olefin})(HI) \quad (VI)$$

Assuming the second term to be small we get

$$-\frac{d(I_2)}{dt} = \frac{k_5K_{3,4}(RH)(I_2)}{(HI)} \quad (VII)$$

Table IV. Application of Equation VII to Runs at Different Temperatures

Run no. (temp, °C)	$(I_2)_0$, Torr	Acrolein, Torr	$\Delta(I_2)$, Torr	$-d(I_2)/dt \times 10^4$, Torr sec^{-1}	$K_5k_{3,4} \times 10^7$, sec^{-1}
Run 3	5.14	135	0.84	2.77	8.0
(214.5)			1.03	2.27	8.4
			1.22	2.12	9.7
			1.40	1.92	10.7
			1.66	1.48	10.45
			1.89	1.02	8.8
Run 30	8.9	97.5	1.67	7.7	36.4
(229.5)			2.01	6.65	39.6
			2.34	5.65	41.5
			2.67	4.52	40.0
Run 36	10.5	55	1.72	17.8	128
(246.5)			2.12	15.9	147
			2.74	11.9	154
			3.14	9.1	142

This equation enables the calculation of $k_5K_{3,4}$ (assuming $(HI) = 2\Delta(I_2)$) and the results for run 25 are given in the last column of Table III. These results show that the same value, within experimental error, is obtained for different extents of the reaction, indicating that eq VII is the right one for the case of iodine + acrolein. A further test is to find if this equation would hold for different temperatures and to study the temperature dependence of $k_5K_{3,4}$ and to see if this dependence makes sense compared to known reactions. Table IV gives the results of the application of eq VII to different extents of the reaction for different temperatures. Table V shows this product $k_5K_{3,4}$ to be independent of the initial concentration of the reactants and gives all the data for the temperature dependence. The least-squares Arrhenius plot for $k_5K_{3,4}$ is shown in Figure 2, $\log(k_5K_{3,4}/\text{sec}^{-1}) = (13.6 \pm 0.4) - (43.9 \pm 0.8)/\theta$ where θ is $2.303RT$ kcal mol^{-1} and the quoted errors are the standard deviations (the correlation coefficient of the line is 0.997). $K_{3,4}$ can be estimated by assuming the same thermodynamic values as for the reaction of iodine with acetaldehyde[16]

$$I_2 + CH_3CHO \overset{K}{\rightleftharpoons} CH_3COI + HI$$

for which it has been found (after correction to 495°K) that

$$\log K = (0.86 \pm 1.0)/4.575 - (1.11 \pm 0.50)/\theta$$

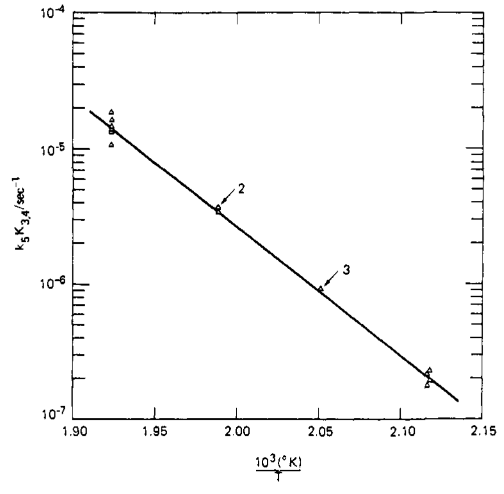

Figure 2. Arrhenius plot for the reaction $I_2 + CH_2CHCHO \rightleftharpoons CH_2CHCOI + HI$ ($K_{3,4}$), $CH_2CHCOI \rightarrow CH_2{=}C{=}CO + HI$ (k_5). Numbers indicate number of overlapping points.

Table V. Dependence of $k_5K_{3,4}$ on the Temperature

Temp, °C (°K)	$(I_2)_0$, Torr	Acrolein, Torr	Range of $-d(I_2)/dt$,[a] Torr sec^{-1}	$10^7 \times k_5K_{3,4}$,[b] sec^{-1}
199.0	2.90	264	$6.37–16.8 \times 10^{-3}$	2.28
(472.1)	3.44	581	$9.9–31.4 \times 10^{-5}$	1.92
199.4	2.96	593	$1.49–2.56 \times 10^{-4}$	2.12
(472.5)	7.45	650	$1.71–3.29 \times 10^{-4}$	1.74
214.5	5.14	135	$1.02–2.77 \times 10^{-4}$	9.35
(487.6)	17.2	540	$4.0–16.8 \times 10^{-4}$	9.45
	20.8	696	$8.75–22.4 \times 10^{-4}$	9.35
229.5	8.9	97.5	$4.52–8.35 \times 10^{-4}$	37.3
	14.2	107	$3.62–10.6 \times 10^{-4}$	37.0
(502.6)	18.1	354	$1.52–2.72 \times 10^{-3}$	34.0
246.5	9.5	128	$1.62–3.38 \times 10^{-3}$	162
(519.6)	10.5	55	$9.1–17.8 \times 10^{-4}$	143
	13.7	59	$1.19–1.87 \times 10^{-3}$	135
	21.3	162	$4.25–6.55 \times 10^{-3}$	184
	21.4	59.1	$9.1–20.1 \times 10^{-3}$	110
	23.0	102	$2.48–3.32 \times 10^{-3}$	138

[a] The range of $-d(I_2)/dt$ from which $k_5K_{3,4}$ was calculated. [b] Calculated according to eq VII.

Assuming the same value for $K_{3,4}$ (assumption of bond additivity for thermodynamic properties) gives $\log k_5 = (13.4 \pm 1.0) - (42.8 \pm 1.0)/\theta$. This value can be compared with the values of other HI elimination reactions[21] $\log k = 13.36 - 50/\theta$, $13.53 - 45/\theta$, $13.65 - 44.7/\theta$, and $13.73 - 38.1/\theta$ for ethyl iodide, isopropyl iodide, 2-iodobutane, and *tert*-butyl iodide, respectively.

Obtaining the value of k_5, it is vital to check if the basic assumption for deriving eq IV, *i.e.*, $k_{-5} < k_{-4}(I)$, is right. k_{-4} can be estimated by assuming that this rate constant is equal to the one for the same reaction with

$$I + CH_3COI \xrightarrow{k} CH_3\dot{C}O + I_2$$

acetyl iodide for which the rate constant was measured[22] as $\log(k/M^{-1}\ \text{sec}^{-1}) = 10.9 - 14.6/\theta$. The average concentration of the iodine is 3.10^{-8} *M*; thus at 495°K (the average temperature) $k_{-4}(I) = 10^{-4.3}$ sec^{-1} while $k_5 = 10^{-5.5}$ sec^{-1} justifying the neglect of k_5 relative to $k_{-4}(I)$.

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(21) S. W. Benson and H. E. O'Neal, "Kinetic Data on Gas Phase Unimolecular Reactions," NSRDS-NBS Report No. 21, National Bureau of Standards, Washington, D. C., 1970, pp 105-108.

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