

581. The Reactions of Methyl and Ethyl Radicals with Hydrogen Bromide and the Strength of C-H Bonds.

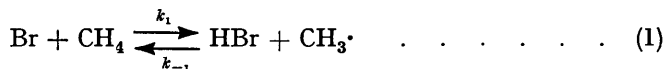
By G. C. FETTIS and A. F. TROTMAN-DICKENSON.

Acetone and ethyl methyl ketone have been photolysed in the presence of hydrogen bromide and iodine. The relative rates of attack by the alkyl radicals on the additives have been found, and the activation energies and heats of reactions calculated. Thence it is found that $D(\text{Me-H}) = 103.9$ and $D(\text{Et-H}) = 98.2$ kcal. mole⁻¹ at 25°, and it is suggested that $D(\text{Pr}^1\text{-H}) = 94.5$ and $D(\text{Bu}^t\text{-H}) = 91.4$ kcal. mole⁻¹.

THE accepted value, 102.5 kcal. mole⁻¹ at 25°, of the dissociation energy of the C-H bond in methane is based on studies of bromination and electron impact,¹ agreement between results of the two methods being good. Consequently $D(\text{CH}_3\text{-H})$ is often regarded as known to a greater accuracy than could be claimed for either of the methods alone. Determination of the bond strength by bromination is based on the equation:

$$D(\text{CH}_3\text{-H}) = D(\text{H-Br}) + E_1 - E_{-1}$$

where E_1 is the activation energy of the forward and E_{-1} of the back-reaction:



E_1 is accurately known; E_{-1} is less certain. Two attempts^{2,3} have been made to relate E_{-1} to E_2 which is the activation energy of the reaction:



It is widely accepted that this reaction has no activation energy, so that $E_{-1} - E_2 = E_{-1}$. Both attempts depended on the photolysis of methyl iodide as the source of radicals.

¹ Cottrell, "The Strengths of Chemical Bonds," Butterworths, London, 1960.

² Andersen and Kistiakowsky, *J. Chem. Phys.*, 1943, **11**, 6.

³ Williams and Ogg, *J. Chem. Phys.*, 1947, **15**, 696.

Consequently the products of reaction (2) could not be determined directly: they had to be inferred from observation of the dependence of the yield of methane on the concentrations of hydrogen bromide and iodine.

The advent of gas chromatography has simplified the determination of methyl iodide in the presence of material of similar boiling point. k_{-1}/k_2 can now be found from the relation:

$$\frac{k_{-1}}{k_2} = \frac{d[\text{CH}_4]/dt \cdot [\text{I}_2]}{d[\text{CH}_3\text{I}]/dt \cdot [\text{HBr}]},$$

when the radicals are formed by the photolysis of acetone in the presence of hydrogen bromine and iodine. If only a small proportion of the reagents is consumed, then

$$\frac{k_{-1}}{k_2} = \frac{(\text{CH}_4)}{(\text{CH}_3\text{I})} \cdot \frac{[\text{I}_2]}{[\text{HBr}]},$$

where the first term is the ratio of the total amounts of methane and of methyl iodide formed.

Much less is known about ethyl radicals. E_1^* for the attack of a bromine atom on ethane has only recently been reliably measured.^{4,5} No measurement of E_{-1}^* has been reported. However, a relation analogous to that above may be derived for ethyl radicals produced by photolysis of ethyl methyl ketone.

EXPERIMENTAL

Apparatus.—The quartz reaction vessel (600 c.c.) was attached to a conventional high-vacuum apparatus. It was contained in an electric furnace into which light from a 125 w mercury arc was focused by a quartz lens. Part of the connecting tubing was wound with heating ribbon to prevent condensation of iodine vapour. Stopcocks were lubricated with silicone grease.

Materials.—Reagent-grade iodine was sublimed twice over potassium iodide and thoroughly degassed. Acetone and ethyl methyl ketone were commercial samples. Hydrogen bromide was prepared by the action of bromine on tetralin, catalysed by powdered aluminium.

Procedure.—Iodine was introduced into the reaction vessel to a pressure determined by the temperature of the water-bath surrounding the storage vessel. Ketone, followed by hydrogen bromide, was measured on a mercury manometer. At the end of the reaction the contents of the cell were distilled through an absorption tube into the chromatography trap. With ethyl methyl ketone, the tube was packed with 3'' of potassium thiosulphate crystals, 2'' of 30% calcium carbonate-ethylene glycol on firebrick (25–52 mesh), and 1'' of magnesium perchlorate to remove iodine, hydrogen bromide, and water. With acetone, the iodine was removed by 40% sodium thiosulphate–firebrick (40–60 mesh) (heated to coat the firebrick), and the hydrogen bromide was adsorbed by an alumina column which was frequently changed.

The products of the ethyl radical reactions were separated on split columns of 3' Celite (80–100 mesh) + 20% of diethyl phthalate (35°) and 2½' alumina (40–60 mesh) at 0°. The products of methyl radical reactions were separated on 6½' Celite (40–60 mesh) + 18% of diethyl phthalate at 30° and 3' of activated charcoal (60–80 mesh) at room temperature. When the charcoal column was by-passed, the gas flowed through a column of glass beads of equal resistance. The carrier gas was hydrogen. The detector was a thermal conductivity cell.

RESULTS AND DISCUSSION

The results for methyl and ethyl radicals are given in Tables 1 and 2. Least-squares treatment yields, for methyl radicals:

$$\log (k_{-1}/k_2) = (-0.300 \pm 0.131) - (1370 \pm 261/2.3RT),$$

and for ethyl radicals:

$$\log (k_{-1}^*/k_2^*) = (0.228 \pm 0.036) - (2.288 \pm 80/2.3RT).$$

⁴ Fettis and Trotman-Dickenson, *J. Amer. Chem. Soc.*, 1959, **81**, 5260.

⁵ Fettis, Knox, and Trotman-Dickenson, *J.*, 1960, 4177.

The extrapolated value for k_{-1}/k_2 at 60° is 0.063, in excellent agreement with the mean value 0.055 found by Andersen and Kistiakowsky.² The agreement with Williams and Ogg's value,³ 0.042, at 140° is less good (0.095).

TABLE 1. *The reactions of methyl radicals with iodine and hydrogen bromide.*

Temp.	I ₂ (mm.)	HBr (cm.)	Me ₂ CO (cm.)	$k(\text{MeI})$ $\bar{k}(\text{MeH})$	Temp.	I ₂ (mm.)	HBr (cm.)	Me ₂ CO (cm.)	$k(\text{MeI})$ $\bar{k}(\text{MeH})$
80°	4.57	3.95	4.90	23.48	164°	4.57	6.02	5.00	18.75
80	"	4.07	4.75	23.44	164	"	4.60	5.38	16.14
80 -	"	4.40	5.25	24.95	164	"	7.37	6.48	14.68
112	"	4.40	4.88	18.11	164	"	4.70	3.30	18.32
112	"	5.46	7.04	19.17	244	"	5.10	4.88	12.64
112	"	4.40	4.80	16.39	244	"	4.95	4.90	12.67
112	2.24	4.74	4.10	19.80	244	"	3.65	5.40	15.10
164	4.57	4.55	4.80	18.45	244	"	2.15	6.50	12.05
164	"	4.45	5.05	15.08	288	"	5.10	5.30	10.00
164	"	5.28	4.90	17.05	288	"	4.70	5.30	10.00
164	"	5.83	3.94	13.41	288	"	4.40	6.40	10.78
164	"	4.98	5.91	16.57	288	8.61	3.60	3.18	11.81

* Pyrex filter used.

Fettis, Knox, and Trotman-Dickenson⁵ found that E_1 for methane is 18.25 kcal. mole⁻¹ and E_1^* for ethane is 13.40 kcal. mole⁻¹.

The mean temperature of the methane reactions was sufficiently close to 460° K for both the forward and the reverse reaction for us to be able to write:

$$D(\text{CH}_3\text{-H})^{460} = D(\text{H-Br})^{460} + E_1 - E_{-1} = 87.9 + 16.95 = 104.85 \text{ kcal. mole}^{-1}.$$

$D(\text{H-Br})^{460}$ is obtained from the value of 103.9 kcal. mole⁻¹ at 0° K.

Hence $D(\text{CH}_3\text{-H})^{298} = 98.2 \text{ kcal. mole}^{-1}$.

Similarly $D(\text{C}_2\text{H}_5\text{-H})^{298} = 98.2 \text{ kcal. mole}^{-1}$.

TABLE 2. *The reactions of ethyl radicals with iodine and hydrogen bromide.*

Temp.	I ₂ (mm.)	HBr (cm.)	COEtMe (cm.)	$k(\text{EtI})$ $\bar{k}(\text{EtH})$	Temp.	I ₂ (mm.)	HBr (cm.)	COEtMe (cm.)	$k(\text{EtI})$ $\bar{k}(\text{EtH})$
54.5°	2.24	4.20	4.95	39.93	119.2°	4.57	4.48	4.36	23.66
59.0	3.24	4.67	4.85	36.93	" ^a	"	4.75	5.05	21.99
65.0	4.57	4.54	4.31	32.28	143.0	"	5.00	5.73	15.85
72.5	"	4.34	4.60	35.14	"	"	4.26	6.42	15.55
73.5	"	3.63	4.55	31.77	"	"	6.10	5.48	19.14
"	"	3.01	4.72	28.70	"	"	3.02	5.64	16.07
74.5	"	3.60	4.85	31.11	"	"	2.23	6.95	17.54
88.0	"	4.79	5.15	26.47	"	2.24	4.94	5.65	17.87
"	"	3.58	6.62	26.98	173.5	4.57	5.80	7.25	14.26
87.5	"	4.28	4.26	24.97	175.0	8.61	5.85	7.85	14.06
"	"	4.74	4.42	30.15	"	4.57	5.11	6.18	14.35
89.0	"	5.56	3.87	27.05	"	8.61	6.38	7.85	11.61
"	"	6.03	3.15	28.27	"	4.57	4.50	6.95	15.40
"	"	3.29	3.30	26.83	"	8.61	4.78	7.35	11.40
101.5	"	3.81	4.57	25.24	179.0	4.57	4.04	6.48	15.98
"	"	3.70	4.67	24.71	"	"	5.46	6.72	16.37
114.5	"	4.45	4.82	20.93	"	"	5.96	7.49	16.44
"	"	4.90	5.45	22.91					
"	"	4.76	2.84	22.80					
"	"	4.70	4.25	22.35					

* Pyrex filter used.

In both instances it was assumed that the heat capacities of the hydrocarbon and its radical were identical.

The difference between the above value and that found for $D(\text{CH}_3\text{-H})$ by Kistiakowsky and Van Artsdalen⁶ arises mainly from three causes. The first, which is independent

* Kistiakowsky and Van Artsdalen, *J. Chem. Phys.*, 1944, **12**, 469.

of kinetic work, is that a higher value for $D(\text{H}-\text{Br})$ has been adopted: the higher value has been universally accepted in recent years. The second reason is that 18.25 kcal. mole⁻¹ rather than 17.8 kcal. mole⁻¹ has been taken for E_1 . The difference arises because we have adopted the simple Arrhenius definition of the activation energy, whereas Kistiakowsky and Van Artsdalen used a "collision theory" activation energy derived from the equation, $k = BT^{\frac{1}{2}} \exp(-H/RT)$. The Arrhenius equation is known to be inadequate, but so also is the collision form. It seems best to use the simpler equation in this case. Unfortunately the errors consequently introduced into E_1 and E_{-1} do not cancel because E_{-1} is not found absolutely but only in terms of E_2 . The third and most direct reason is that we have measured $E_{-1} - E_2$ and found it to be 0.7 kcal. mole less than the value of E_{-1} assumed by Kistiakowsky and Van Artsdalen.⁶

The probable errors in the present determination of the bond strengths are of three kinds. First are those that can be evaluated statistically, arising from the limitations of our measurements. For ethane they are very small: $E_1^* = 13.40 \pm 0.09$ and $E_{-1}^* - E_2^* = 2.29 \pm 0.08$; for methane, $E_{-1} - E_2 = 1.3 \pm 0.3$. The error in E_1 cannot be readily found but the independent determination by Kistiakowsky and Van Artsdalen is in complete agreement with that given here. The second kind of error arises because both E_1 and E_1^* are ultimately based on Kistiakowsky and Van Artsdalen's activation energy for the attack of bromine atoms on methyl bromide. It should be noted that this uncertainty does not affect the determination of $D(\text{CH}_3-\text{H}) - D(\text{C}_2\text{H}_5-\text{H})$. The third kind of error arises from the uncertainty of the activation energies for the attack of radicals on iodine. We have accepted the view that it is zero. The best evidence for this value is Christie's work⁷ on the comparison of the rates of reaction of methyl radicals with oxygen and iodine. She found that at room temperature $k_2 = 10^{13}$ mole⁻¹ c.c. sec.⁻¹ and remarked that this value is consistent with a steric factor of unity and a low activation energy. Rough calculations on the basis of the theory of absolute reaction rates, which has been successful in predicting the A factors of alkane-halogen reactions,⁸ indicate that A_2 should lie between $10^{11.5}$ and $10^{12.5}$ mole⁻¹ c.c. sec.⁻¹. Accordingly the evidence in favour of $E_2 = 0$ is better than Christie suggests. If E_2 is greater than this, then the calculated bond strengths are too high. It seems reasonable to attach errors of ± 1 kcal. mole⁻¹ to the bond strengths found here and smaller errors, say 0.3 kcal. mole⁻¹, to the important bond-strength differences. The overall error is close to that usually quoted, but the values are likely to be more reliable.

Although this work provides direct evidence on the strengths of only methyl and ethyl bonds some conclusions can be drawn about the C-H bonds formed by other alkyl radicals. Fettes and Trotman-Dickenson⁴ deduced values (α) of $D(\text{R}-\text{H})$ shown in Table 3 from the activation energy (E) for the attack of bromine atoms on the alkanes, and the Polanyi relation $E = \alpha\Delta H + c$. The most probable value of α is 0.86. These values can now be

TABLE 3. $D(\text{R}-\text{H})$ for alkanes at 25° (all kcal. mole⁻¹).

Alkyl	E	Polanyi relation		This work	Electron-impact	$\Delta H_f^\circ(\text{R})$
		(α)	(b)			
Methyl.....	18.3	102.5	103.9	103.9	103.4	33.9
Ethyl	13.4	96.9	98.3	98.2	98.3	26.0
Neopentyl	14.3	97.9	99.3	—	—	7.5
Isopropyl	10.2	93.1	94.5	—	95.3	17.6
s-Butyl	10.2	93.2	94.6	—	—	12.3
t-Butyl	7.5	90.0	91.4	—	91.0	7.1

corrected (b) to correspond to the new value of $D(\text{CH}_3-\text{H})$. The agreement between $D(\text{C}_2\text{H}_5-\text{H})$ from the Polanyi relation and that found here is good. The agreement with the electron-impact values is also good. These bond strengths have been obtained from

⁷ Christie, *Proc. Roy. Soc.*, 1958, *A*, **244**, 411.

⁸ Fettes, Knox, and Trotman-Dickenson, *Canad. J. Chem.*, 1960, **38**, 1643.

those usually accepted for 0°K.^1 The last column of the Table lists the heats of formation of the radicals at 25° , from which many bond strengths can be derived.

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CHEMISTRY DEPARTMENT, EDINBURGH UNIVERSITY.

[Present address (A. F. T.-D.): EDWARD DAVIES CHEMICAL LABORATORY,
ABERYSTWYTH.]

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