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The kinetics of the photochemical bromination of ethane was determined. The mechanism is very similar to the analogous brominations of hydrogen and methane:

$$(1) \qquad Br_2 + h\nu = Br + Br$$
$$(2) \qquad Br + C_2H_6 = C_2H_5 + HBr$$
$$(3) \qquad C_2H_5 + Br_2 = C_2H_5Br + Br$$
$$(4) \qquad C_2H_5 + HBr = C_2H_6 + Br$$
$$(5) \qquad Br + Br + M = Br_2 + M.$$

Rate constants computed by assuming various efficiencies for ethane as the third body in step (5) are presented, as well as those calculated by considering heterogeneous recombination of bromine atoms. The rate of bromination of ethyl bromide is about the same as that for ethane, but its exact determination was precluded by the presence of rapidly brominated impurities. The experimental activation energy, 13.6 ± 0.5 kcal., is quite insensitive to the several variations in mechanism discussed, and indicates a value of 98 ± 2 kcal. for the upper limit of the strength of the $C_2H_5 - H$ bond. This figure is in good agreement with absolute values reported by other workers.

KINETIC studies of the bromination of methane[1] having proved successful, it was decided to extend the method to ethane.

EXPERIMENTAL

Ethane was prepared by catalytic hydrogenation with cobalt-nickel catalyst of 99.5 percent ethylene, a standard product of the Ohio Chemical Company. The hydrogen was purified carefully to remove traces of oxygen and passed through in twofold excess. Any unsaturates remaining after the hydrogenation were removed by fuming sulfuric acid; potassium hydroxide was used to free the ethane from acid gases. The ethane was condensed in liquid nitrogen. It was then given a batch distillation with efficient stirring followed by several bulb-to-bulb distillations under high vacuum to remove permanent gases and passed through a glass wool filter at dry ice temperature to remove mercury. Purity tests described by Nickle,[2] indicated about 0.01 percent unsaturates, as ethylene, and 0.02 mole percent high boiling material, calculated as butane. The ethane registered an equilibrium pressure of 0.02 mm Hg when immersed in liquid air. (Compare Kistiakowsky and Nazmi:[3] 0.95 $\times 10^{-2}$ at liquid oxygen temperature.)

Two samples of ethyl bromide were used. The first sample was prepared from Baker's "purified" ethyl bromide by distilling through a 9-foot glass-helix packed column and recovering the fraction boiling at 38.6–38.8°C. This fraction was further purified by three bulb-to-bulb high vacuum distillations. It had to be stored behind a stopcock lubricated with Shawinigan low melting resin because of solubility in ordinary grease. The second sample was prepared from the same "Purified" grade by treatment with liquid bromine for one-half hour, subsequent removal of bromine by 20 percent sodium hydroxide and drying of the product over calcium bromide. The dried material was distilled as above; a fraction boiling at 38.4–38.5° being redistilled and a middle cut boiling at 38.3° (758 mm corr.) taken for final bulb-to-bulb vacuum distillation. It was stored behind a glass valve. It will be shown that

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[1] G. B. Kistiakowsky and E. R. Van Artsdalen, J. Chem. Phys. 12, 469 (1944), hereafter termed I.

[2] A. G. Nickle, Thesis (Harvard University, 1941).

[3] G. B. Kistiakowsky and F. Nazmi, J. Chem. Phys. 6, 18 (1938).

these samples of ethyl bromide apparently contained appreciable amounts of impurity, probably ethanol.

Bromine and hydrogen bromide were prepared and purified as described in I.

The experimental method was essentially the same as described in I. However, one important change was made. Small pressures were measured with the quartz spiral null-point manometer against a butyl-phthalate manometer instead of a mercury manometer. Special pains were taken to outgas the butyl-phthalate thoroughly before each set of measurements. Butyl-phthalate pressures were converted to mm of mercury employing measured absolute densities of the butyl-phthalate over the temperature range 20–31°C.

In the kinetic experiments, partial pressures of bromine were measured after various periods of illumination. The rate of reaction was determined over the first ten percent of reaction only, during which interval interference by products of reaction is at a minimum. It was found that the rate during the first ten percent was practically linear. Constants in this paper properly are termed initial constants in the same way as those cited in I.

RESULTS

Bromination of ethane conceivably could lead to a considerably greater diversity of products than in the case of bromination of methane. It was necessary to prove the assumption that during the first 10 percent of reaction essentially only ethyl bromide is formed by photo-bromination of ethane. For this purpose a 2-liter mixture of 43.5 mm of bromine and 495 mm of ethane was illuminated until reaction was practically complete and an analysis made of the reaction products. From average determinations of vapor pressure and refractive index it was concluded that the product of reaction consisted of a minimum of 65 percent of ethyl bromide. Under the experimental conditions employed this corresponds to a minimum of 97 percent of ethyl bromide during the first 10 percent of reaction. It was on this basis that constants were calculated from rates during the initial 10 percent of reaction.

The measured thermal, or "dark," rate of

TABLE I. Photobromination of ethane.

Temp. (°C)	Initial pressure (mm at t°C) Br_2	C_2H_6	Measured rate (mm/min.)	k	k' (sec.$^{-1}$×10^5)	k''
					(corrected to 89.8°)	
90.1	17.40	660.0	10.4	161	44	174
89.6	17.38	608.8	9.3	155	43	172
90.2	17.64	319.6	5.92	132	42	174
89.4	16.52	317.1	6.11	147	46	183
89.9	16.35	310.0	5.69	136	43	166
					(corrected to 59.7°)	
59.9	32.7	664.9	2.18	25	7.6	26
59.4	14.7	648.0	1.60	28	7.4	30
59.3	15.25	733.5	1.63	26	6.9	28
59.5	9.48	721.8	1.70	34	8.6	37
59.7	9.52	741.4	1.99	39	9.8	42
59.5	16.82	288.5	1.09	27	8.6	33
59.1	16.05	288.2	.96	25	7.8	31
59.1	15.92	287.8	1.06	28	8.7	35
60.1	15.9	290.4	1.10	27	8.4	36
60.2	10.82	278.5	.98	29	8.5	39
59.7	31.42	174.1	.81	20	8.7	26
58.6	29.55	188.2	.77	20	8.3	26
59.5	16.2	187.4	.76	24	8.5	36
59.9	9.80	192.8	.72	28	8.5	47
59.3	30.52	53.5	.226	12	7.4	31
					(corrected to 35.6°)	
35.1	14.1	272.3	.17	4.7	1.5	6.3
35.2	14.80	282.1	.221	5.9	1.88	7.4
36.7	14.68	281.5	.231	5.6	1.77	7.5
35.4	14.50	274.6	.213	5.8	1.82	7.8

bromination at 96°C was 0.02 mm/min. Such "dark" reaction was negligible, since rates of photobromination were of the order of 5–10 mm/min. at 90°C.

If bromination of ethane, in its early stages, involves a mechanism analogous to that for bromination of methane, the rate of the photochemical reaction should be proportional to the square root of light intensity. An experiment performed to check this gave fair agreement with prediction (observed rate = 0.62 mm per min.; calculated rate = 0.70 mm per min.), but indicated that the rate probably depends upon a power of the light intensity between 0.5 and 1.

Data for a series of experiments at three mean temperatures are presented in Table I. All rate constants in this paper have been corrected to mean temperatures with the aid of temperature coefficients calculated from the experimentally evaluated activation energy. The coefficients were 1.073 at 35°, 1.062 at 60°, and 1.052 at 90°. This procedure will be justified later when it will be shown that the activation energy is only slightly subject to the "constant" used in calculating it. The corrections rarely exceeded 2 percent.
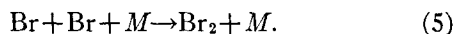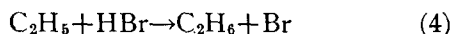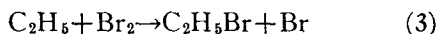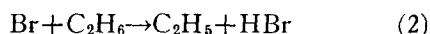
k was calculated from the following rate

equation in analogy with the methane-bromine reaction.

$$\frac{-d[Br_2]}{dt} = \frac{d[C_2H_5Br]}{dt} = \frac{k[C_2H_6][Br_2]^{\frac{1}{2}}}{[P]^{\frac{1}{2}}} \quad (A)$$

where P = total pressure. This equation is valid for initial rates only, where reaction products do not interfere.

Definite trends are observed in k, *viz.*, decreasing k with decreasing ethane pressure and increasing k with decreasing bromine pressure, indicating that the power of ethane concentration should be greater than one and that of bromine less than 0.5. Let us consider the following reaction mechanism in analogy with the bromination of methane.

$$Br_2 + h\nu \rightarrow Br + Br \quad (1)$$

$$Br + C_2H_6 \rightarrow C_2H_5 + HBr \quad (2)$$

$$C_2H_5 + Br_2 \rightarrow C_2H_5Br + Br \quad (3)$$

$$C_2H_5 + HBr \rightarrow C_2H_6 + Br \quad (4)$$

$$Br + Br + M \rightarrow Br_2 + M. \quad (5)$$

Equation (A) can be derived from this mechanism for the condition that $[HBr] = 0$. $k = k_2(k_{ap}\alpha I/k_5)^{\frac{1}{2}}$ where α = absorption coefficient, I is the incident light intensity, and k_{ap} is a temperature independent apparatus constant. Two effects may be important in accounting for the observed trends in k, namely, different efficiencies of molecules in promoting reaction (5) and heterogeneous reaction.

If the efficiency of the third body M in reaction (5) is not the same for all molecules in the reacting system the rate of this reaction will not be given by $k_5[M][Br]^2$ but rather by a summation over individual effects of the various molecular species, such as $k_5[nA + nB + \cdots][Br]^2$. That different molecules have different efficiencies in this respect is well known,[4] and has been demonstrated in the case of the methane reaction.[1] However, it is quite general that more complicated molecules are better able to absorb translational energy of colliding bromine atoms than are simpler molecules, methane being shown to be more effective than hydrogen. The derivation of the rate equation is such that ethane would have to be considered less efficient than bromine to account for the observed effect. By assuming that each three-body collision between two bromine atoms and a bromine molecule is as effective as n such collisions in which ethane is the third body the following rate expression is derived when no HBr is present.

$$\frac{-d[Br_2]}{dt} = \frac{k'[Br_2]^{\frac{1}{2}}[C_2H_6]}{\left([Br_2] + \dfrac{[C_2H_6]}{n}\right)^{\frac{1}{2}}} \quad (B)$$

where $k' = k_2'(k_{ap}\alpha I/k_5)^{\frac{1}{2}}$. The constants k' in Table I have been calculated with $n = 20$ which gave the best set of values. This would indicate that ethane is only about one twentieth as effective a third body as bromine, which is a rather surprising result. It should be noted, however, that fairly large changes in n, e.g., $n = 25$ instead of 20, reflect only moderate changes in k'.

Heterogeneous recombination of bromine atoms on the walls of the reaction vessel would account for a decrease in rate constant with decreasing total pressure. Rabinowitch and Wood[4] have demonstrated this effect, but in general such heterogeneous recombination is not important at pressures above 200 mm, although subject to reaction vessel dimensions and intensity of illumination. It is possible to make an empirical correction for the wall reaction. We add to the above reaction scheme the following recombination reaction.

$$Br + Br \xrightarrow{\text{wall}} Br_2. \quad (6)$$
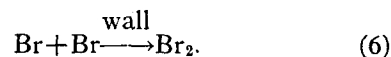
The rate of disappearance of Br atoms is increased by the quantity $2k_6[Br]/[M]$, where k_6 is a constant which depends upon vessel dimensions, diffusion coefficient, etc. The rate of reaction derivable from this scheme for zero HBr concentration is

$$\frac{-d[Br_2]}{dt} = \frac{k''[C_2H_6]\left\{\left(\dfrac{C^2}{[M]^2} + [M][Br_2]\right)^{\frac{1}{2}} - \dfrac{C}{[M]}\right\}}{[M]}, \quad (C)$$

[4] E. Rabinowitch and W. C. Wood, Trans. Faraday Soc. **32**, 907 (1936); E. Rabinowitch and S. C. Lehmann, *ibid.* **31**, 689 (1935).

where $k'' = k_2''(k_{ap}\alpha I)^{\frac{1}{2}}/k_5^{\frac{1}{2}}$ and shows the temperature dependence of bromination, ascribed to k_2, and $C^2 = k_6^2/4k_1k_5$. We are left with an adjustable constant C which was evaluated from two experiments in which total pressure varied by a factor of about 8. The value found was $C = 11$ which was used to compute k'' in Table I. The effect of varying C was tested and found to be small for $C = 9$ and 13. It is observed that this treatment gives good constancy for high and low total pressures, but there is a marked trend toward higher constants for decreasing bromine pressure.

Perhaps a combination of the two modes of correction (varying third-body efficiency and wall recombination) would improve the situation, but the use of two adjustable parameters would be involved and scarcely justified..

Constants calculated according to the three methods outlined above, and presented in Table I, have been used to compute activation energies. Considerations concerning computation of activation energy of photobromination of methane outlined in I are applicable in this case also. The following results were obtained:

from k $E = 13.4 \pm 0.7$ kcal.

from k' $E = 13.3 \pm 0.4$ kcal.

from k'' $E = 14.0 \pm 0.4$ kcal.

The average experimental value, $E = 13.6 \pm 0.5$ kcal., seems quite certain. It is noted that although absolute magnitudes of rate constants calculated by the several methods vary greatly, their temperature coefficients remain practically unchanged. The experimental energy of activation has been corrected to the true value by subtracting the term $\frac{1}{2}RT$ which yields a final value of 13.3 ± 0.5 kcal. Since in the proposed reaction scheme the temperature dependence may be ascribed to the endothermic reaction (2) between Br atoms and C_2H_6 molecules, we have assigned an activation energy of 13.3 kcal. to this reaction.

Various experiments were made to measure the extent of inhibition by HBr, which would occur through reaction (4) $C_2H_5 + HBr \rightarrow C_2H_6 + Br$. The rate equation in the presence of HBr is

$$\frac{-d[\mathrm{Br_2}]}{dt} = \frac{k[\mathrm{Br_2}]^{\frac{1}{2}}[\mathrm{C_2H_6}][1/P]^{\frac{1}{2}}}{1 + \dfrac{k_4}{k_3} \dfrac{[\mathrm{HBr}]}{[\mathrm{Br_2}]}}, \quad (C)$$

where $k = k_2(k_{ap}\alpha I/k_5)^{\frac{1}{2}}$. In actual practice experiments with HBr were made in pairs bracketed alternately between those with no HBr present. Data at three temperatures are presented in Table II. It is evident that inhibition by hydrogen bromide is temperature independent, in contrast with the effect observed in bromination of methane.[1] Temperature independence of the ratio of these two specific reaction rate constants k_4/k_3 indicates that the activation energies of the two reactions are essentially equal. The magnitude of k_4/k_3 is considerably larger than in hydrogen bromide synthesis[5] or methane bromination,[1] from which one may surmise that the steric factors of the two reactions are more nearly equal in the case of ethane than in the case of hydrogen or methane.

A few experiments at 60–61°C were made of

TABLE II. Photobromination of ethane. Inhibition by HBr.

	Initial pressures (mm at t°C)			
t°C	C_2H_6	HBr	Br_2	k_4/k_3
90.0	326.3	102.3	16.2	0.68
89.9	325.7	103.0	16.97	.74
89.8	323.1	103.9	16.39	.68
89.9	312.9	104.0	16.2	.58
89.9	309.5	103.5	16.6	.58
60.6	195.7	98.5	15.40	.64
35.2	266.0	82.8	14.2	.7

the photobromination of ethyl bromide. It was found that there was an extremely rapid initial reaction in which approximately 7 percent of the ethyl bromide appeared to react. This was followed by a nearly linear reaction taking place at a rate about equal to the rate of bromination of ethane under similar conditions. Upon re-admitting fresh ethyl bromide to the reaction mixture a second rapid reaction corresponding to about 7 percent of the readmitted ethyl bromide occurred. The initial rapid reaction was shown also by the sample of ethyl bromide treated with bromine as described above. The literature[6] reveals that ethyl bromide and ethanol form an azeotrope boiling at 37.6° and containing 93 percent ethyl bromide. If our sample of ethyl bromide contained 7 percent ethanol, the initial,
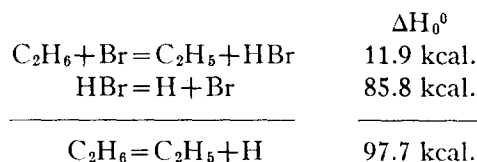
[5] M. Bodenstein and H. Lütkemeyer, Zeits. f. physik. Chemie 114, 208 (1924); M. Bodenstein and S. C. Lind, ibid. 57, 168 (1906).
[6] International Critical Tables, Vol. III, p. 320.

rapid bromination would be explained quantitatively if it is assumed that ethanol is brominated much more rapidly than ethyl bromide. In view of the strength of the $C-OH$ bond (some 30 kcal. less than that of the $C-H$ bond), this is quite plausible. Probably a small amount of oxygen would be released and would be expected to inhibit bromination of ethyl bromide. Therefore no quantitative reliance can be placed on the experiments with ethyl bromide, although they indicate that the rate is not very different from that with ethane.

CARBON-HYDROGEN BOND STRENGTH

It is possible to utilize data presented in this paper to calculate with considerable accuracy the carbon-hydrogen bond strength in ethane. At the mean temperature of the experiments, 333°K, the heat of reaction of $C_2H_6+Br \rightarrow C_2H_5+HBr$ will be the activation energy of the reaction as written, diminished by the activation energy of the reverse, i.e., $13.3-E_4$ kcal. While no measurements of E_4 have been made, it can be estimated with close approximation. In the case of methane,[1] E_4 was shown to be about 1–2 kcal. In general it is known that such reactions occur on almost every collision and require very low energies of activation. We shall assume that in this case $E_4=0.8$ kcal., whence the heat of reaction is 12.5 kcal. at 333°K. This has been recomputed to 0°K by the method described in I, giving $\Delta H_0^0=11.9$ kcal. We now write:

	ΔH_0^0
$C_2H_6+Br = C_2H_5+HBr$	11.9 kcal.
$HBr = H+Br$	85.8 kcal.
$C_2H_6 = C_2H_5+H$	97.7 kcal.

A probable error of about ± 2 kcal. is assigned to this value. We find the following rounded values of this $C-H$ bond strength

°K	$D_{(C_2H_5-H)}$
0	98 kcal.
298	99 kcal.

Steacie and Phillips[7] have estimated the $C-H$ bond in ethane to be 95 kcal., while Stevenson[8] has obtained the value of 96 kcal. from electron impact potentials. Our value of 98 kcal. would approach these more closely if it should develop that the activation energy of reaction (4) were larger than 1 kcal.

Comparison with the $C-H$ bond strength obtained for methane in I shows that the bond strength of ethane is about 3 kcal. lower, a result one might anticipate. It is interesting that the substitution of either a bromine atom or a methyl radical for an hydrogen atom in methane causes about the same decrease in carbon-hydrogen bond strength.

[7] E. W. R. Steacie and N. W. F. Phillips, J. Chem. Phys. 6, 179 (1938); Can. J. Research B16, 303 (1938).
[8] D. P. Stevenson, J. Chem. Phys. 10, 291 (1942).