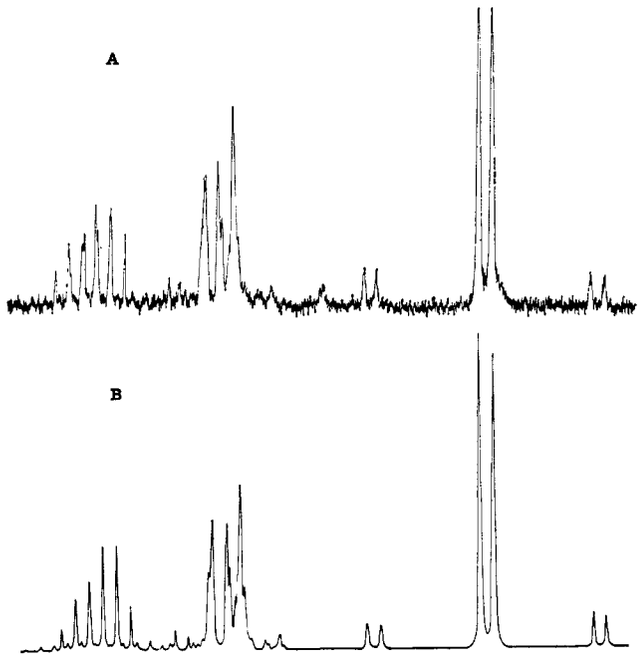

Figure 2.—Experimental proton spectrum (A) of diallylmercury in perdeuteriotetrahydrofuran at 60 MHz and calculated spectrum (B) using the chemical shift and coupling parameters for the 60-MHz analysis as listed in Table I.

Packard 4204A audiooscillator by linear interpolation between TMS side bands. The 100-MHz spectra were obtained on a Varian Associates HA-100 spectrometer operated in the frequency-sweep mode. A Hewlett-Packard V-4315 frequency counter permitted measurement of the line positions to ±0.1 Hz.

Spin decoupling at 100 MHz of nuclei H-4 and H-5 caused simplification of the H-1 multiplet to a symmetrical quartet centered at −599.3 Hz from TMS with a total separation of 27.2 Hz. The spacing of this quartet suggested that J_{12} was about 10 Hz and J_{13} about 17.2 Hz, which values were used as original input in the LAOCOON computer program.

Subsequently, a 220-MHz spectrum of diallylmercury obtained on a Varian Associates HR-220 spectrometer gave essentially first-order resonances of H-2 and H-3 which gave J_{12} and J_{13} as 16.6 and 9.5 Hz, respectively.

TABLE I
CHEMICAL SHIFTS AND COUPLING CONSTANTS IN HERTZ FOR DIALLYLMERCURY (1) IN PERDEUTERIOTETRAHYDROFURAN

	100 MHz[a]	60 MHz[b]
δ_1	598.10	360.24
δ_2	455.38	273.52
δ_3	467.60	281.17
$\delta_4 = \delta_5$	186.48	113.04
J_{12}	9.52[c]	9.43
J_{13}	16.75[d]	17.09
$J_{14} = J_{15}$	8.64	8.81
J_{23}	2.21	2.21
$J_{24} = J_{25}$	−0.66	−0.63
$J_{34} = J_{35}$	−1.04	−0.98
J_{16}[e]		45.85
J_{26}[e]		48.82
J_{36}[e]		49.96
J_{46}		144.30[f]

[a] At 32°. [b] At ~37°. [c] 9.5 Hz from the 220-MHz spectrum. [d] 16.6 Hz from the 220-MHz spectrum. [e] 8.1 Hz at −16.5° and 8.0 Hz at −38°. [f] 147.0 Hz at −16.5° and 147.5 Hz at −38°.

Registry No.—Diallylmercury, 2097-71-4.

Acknowledgment.—We thank Professor S. I. Chan for assistance in securing 100-MHz spectra and for valuable suggestions. Mr. J. H. Prestegard obtained the 220-MHz spectrum and carried out the spin-decoupling experiment.

Bromine Addition to Olefins in Aqueous Solution

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Rates of addition of bromine to methyl acrylate, methyl crotonate, methyl methacrylate, and acrylamide in aqueous solutions have been measured electrometrically in the presence of added bromide at 20, 30, and 40°. The rate constants for addition of Br_2 as well as of Br_3^- have been calculated and hence the corresponding values of activation energy and entropy of activation have been computed for each reaction. The relative reactivities of the four olefins follow the same order (methacrylate > crotonate > acrylamide > acrylate) with respect to both bromine and tribromide ion. For reaction with bromine, activation energy as well as frequency factor lies in the order acrylate > crotonate > acrylamide > methacrylate. For tribromide ion, activation energy lies in the order acrylamide > methacrylate > acrylate > crotonate, the sequence for the frequency factor being acrylamide > methacrylate > crotonate > acrylate. The results are not strictly in conformity with what should be expected from structural considerations.

Rates of addition of bromine to several olefins in aqueous solutions were measured by Kanyaev[1,2] and he concluded that the relative reactivity of molecular bromine and tribromide ion varies continuously with the reactivity of the olefin and also that the proportion of the dibromide in the product is equal to the fraction of reaction effected by tribromide ion. No support for this view has been provided by the studies of Atkinson and Bell.[3] From their kinetic results, coupled with product analysis, Atkinson and Bell postulated a general mechanism which is consistent with their findings. More recently Bell and Pring[4] have reported the kinetic results for addition of bromine to some more olefins in aqueous solution in the presence of added chloride and bromide, which tend to substantiate their earlier conclusions. In general, the velocity constants for reaction with bromine or tribromide ion, varying over eleven powers of ten, show an approximate correlation with the Taft σ^* substituent constants.

The object of the present investigations was to determine the activation energy and the entropy of activation for the reaction with bromine as well as

(1) N. P. Kanyaev, *J. Gen. Chem. USSR*, **26**, 3037 (1956).
(2) N. P. Kanyaev, *ibid.*, **29**, 825 (1959).
(3) J. R. Atkinson and R. P. Bell, *J. Chem. Soc.*, 3260 (1963).
(4) R. P. Bell and M. Pring, *ibid.*, *B*, 1119 (1966).

tribromide ion, for four olefinic substances, from rate measurements at different temperatures. These values should be more useful in providing some insight into the reaction mechanism than relative reactivities alone.

Experimental Section

Materials.—The samples of methyl acrylate (Light & Co., England) and methyl methacrylate (National Chemical Laboratory, Poona, India) were purified by the usual procedure.[5] Methyl crotonate (*trans*) was prepared and purified by the general method.[6] After drying with calcium chloride, the samples were fractionally distilled in an all-glass apparatus, the middle fraction being collected for the work. Acrylamide (Eastman Kodak Co.) was recrystallized from chloroform and dried before use. Inorganic reagents were of G. R. grade (E. Merck). All solutions were made with water which had been redistilled from alkaline potassium permanganate.

The initial concentrations of the olefinic compounds in the reaction mixtures were in the range 5×10^{-3} to 1.25×10^{-2} M for methyl crotonate and acrylamide, 2×10^{-2} to 1×10^{-1} M for methyl acrylate, and nearly 5×10^{-3} M for methyl methacrylate.

Initial bromine concentrations in the reaction mixtures were in the range 6×10^{-4} to 6×10^{-3} M, being about 5–10 times lower than the concentration of the olefinic compound in the reaction mixture.

Perchloric acid concentration was at 0.1 M. The only purpose of using the acid was to maintain the reaction conditions similar to those used by Bell and Atkinson[3] in their studies. They have, however, shown that the acid does not affect the kinetic results. In the presence of 0.1 N perchloric acid, hydrolysis of acrylamide might occur. To investigate this point, 0.01 M acrylamide in 0.1 N perchloric acid was kept overnight at room temperature, and a portion of the mixture was then made just alkaline and treated with Nessler reagent. The test showed absence of ammonia, indicating that hydrolysis of the amide does not occur under the conditions. In alkaline medium however, hydrolysis readily occurs as shown by the Nessler test. Further, in acid medium, any reaction of bromine on the nitrogen of the amide, forming bromamide, is ruled out, so that bromine only adds to the carbon–carbon double bond.

Each reaction was studied with different bromide concentrations (0.02–0.2 M).

Kinetic Measurements.—Kinetic measurements were carried out at 20, 30, and 40° (temperature variation ±0.1°) under dark conditions. The reaction was followed electrometrically, the method adopted being essentially similar to that described by Bell and Ramsden.[7] The reactions were conducted in a cell—a 150-ml beaker tightly closed by a rubber stopper through which were inserted one platinum wire electrode and a dip-type calomel electrode (fibre type, a product of Central Glass and Ceramic Research Institute, Calcutta) ending in a fine capillary tip. Emf measurements were made with a Leeds & Northrup K-type potentiometer and a moving coil galvanometer.

Calculated volumes of perchloric acid, potassium bromide, and bromine solutions were added to the cell vessel which was placed in a thermostat. After some time was allowed the potentiometer readings were noted. When the potentiometer reading became stable, the olefinic compound, kept previously in the same thermostat, was added to the cell vessel by means of a graduated pipet. The final volume of the reaction mixture was usually 40 ml.

The emf plotted against time gave good straight lines over a range of 60 mV, corresponding to a decrease in bromine concentration by a factor of 100. The time taken for this change was 25 to 30 min for methyl acrylate and acrylamide and 5 to 10 min for methyl crotonate and methyl methacrylate. The linearity of the plot of emf against time shows that the reaction is kinetically first order with respect to bromine, being zero order in the olefin which is always present in excess. Typical plots are shown in Figure 1 for illustration.

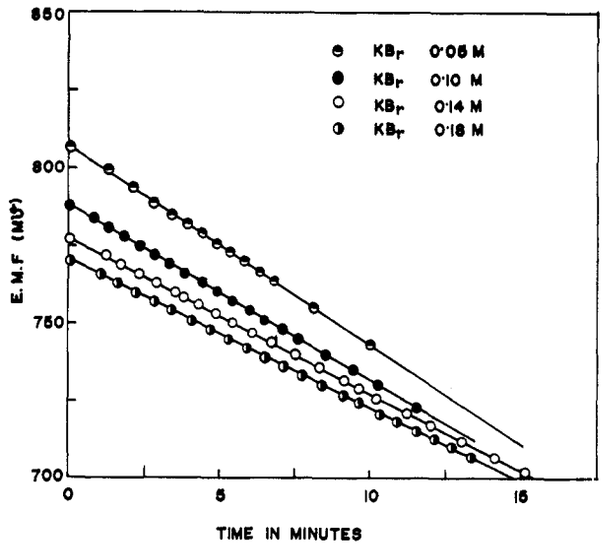

Figure 1.—Bromination of methyl methacrylate (5.0×10^{-3} M) at 20°. The course of a typical experiment.

The second-order rate constants (k) for each reaction at different temperatures have been obtained from eq 1–3 where C is the molar concentration of the olefin.

$$k_{20} = 79.4 \frac{dE}{dt}/C \quad (1)$$

$$k_{30} = 76.8 \frac{dE}{dt}/C \quad (2)$$

$$k_{40} = 74.3 \frac{dE}{dt}/C \quad (3)$$

Results

Assuming that the main product in the reaction between bromine and bromide ion is the tribromide ion and also assuming that Br_2 and Br_3^- are the only brominating species, the observed velocity constant for the bromination of olefin is given[3] by eq 4, where k_1 =

$$k(1 + K[Br^-]) = k_1 + k_1' K[Br^-] \quad (4)$$

second-order velocity constant for the reaction with the species Br_2, k_1' = second-order velocity constant for the reaction with the species Br_3^-, and K, the equilibrium constant, = $[Br_3^-]/[Br_2][Br^-]$. The K values corresponding to the temperatures 20, 30, and 40° are 17.26, 15.89, and 14.69, respectively, as obtained from the linear plot of log K values, as reported by Scaife and Tyrrell,[8] against reciprocals of absolute temperature. Eq 4 predicts a linear relation between the quantity on the left-hand side and the bromide concentration, $[Br^-]$, the values of k_1 and k_1' being obtainable from the intercept and the slope respectively of the straight-line plot. For illustration, the plot for acrylamide is shown in Figure 2.

Table I gives the observed values of the second-order rate constants (k) at different bromide concentrations together with the values of $k(1 + K[Br^-])$. The k_1 and k_1' values are shown in Table II. It should be noted, however, that the equilibrium constant (K) must be subject to salt effects, as also the rate constants (k_1 and k_1'), which have not been considered. Data for salt effects on the tribromide equilibrium are not available. Moreover, Atkinson and Bell[3] found that salt effects on

(5) E. H. Riddle, "Monomeric Acrylic Esters," Reinhold Publishing Corp., 1954.

(6) A. I. Vogel, "A Text Book of Practical Organic Chemistry," Longmans, Green and Co. Ltd., 1956, p 927.

(7) R. P. Bell and E. N. Ramsden, *J. Chem. Soc.*, 161 (1958).

(8) D. B. Scaife and H. J. V. Tyrrell, *ibid.*, 386 (1958).

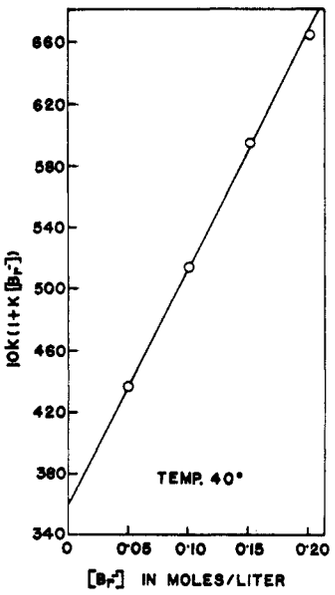

Figure 2.—Bromination of acrylamide.

TABLE I

BROMINATION OF OLEFINS ([H⁺] = 0.10 *M*)

[Br⁻], mol/l.	$10^2 k$, l. mol⁻¹ sec⁻¹ 20°	30°	40°	$10^2 k(1 + K[Br^-])$ 20°	30°	40°
			Acrylamide			
0.05	45.5	112.2	252.5	84.8	201	438
0.10	38.6	92.2	208.0	105.3	239	514
0.15	32.8	81.7	185.8	118.0	277	595
0.20	30.2	76.8	168.4	134.0	321	663
			Methyl Acrylate			
0.02	3.73			5.02		
0.05	3.41	8.63	24.15	6.36	15.5	41.9
0.10	3.18	7.53	20.44	8.66	19.5	50.5
0.14		7.20			23.2	
0.15	3.04		17.95	10.91		57.4
0.18		6.62			26.0	
0.20			16.72			65.9
			Methyl Crotonate			
0.02	82.6			111		
0.05	73.7	189	416	137	339	722
0.10	63.5	158	327	173	410	807
0.15	57.2		282	205		902
0.20		127.5	252		533	992
			Methyl Methacrylate			
0.05	159	384	692	296	689	1200
0.10	151	333	594	410	863	1468
0.14	132			449		
0.15		299	554		1010	1776
0.18	125			532		
0.20		282	535		1177	2107

the observed rate constants are specific so that the problem is not solved by working at a constant ionic strength. Some uncertainties are, therefore, inherent in the values of k_1 and k_1' reported in Table II.

For each olefinic species, the energy of activation for reaction with Br_2 as well as with Br_3^- was obtained by plotting log k_1 and log k_1' against reciprocal of absolute temperature. The plots for acrylamide are shown in Figures 3a and 3b. The entropy of activation ($\Delta S^{\pm}$) at 30° was calculated by equating the experimentally obtained value of the frequency factor A (l. mol^{-1} sec^{-1}) to $e\left(\frac{kT}{h}\right)(e^{\Delta S^{\pm}/R})$. The value of $\Delta S^{\pm}$ so calculated

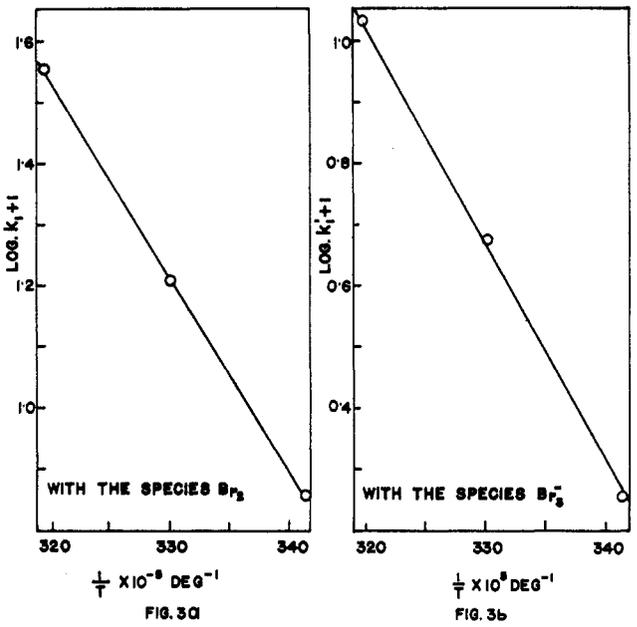

Figure 3.—Dependence of rate constant on temperature for bromination of acrylamide.

refers to the molar scale. The values of activation energy, frequency factor and entropy of activation are shown in Table III.

Discussion

The over-all rates of bromine addition to the three α,β-unsaturated esters lie in the order methacrylate > crotonate ≫ acrylate. The results obtained by Atkinson and Bell[3] with ethyl acrylate and crotonate at 25° are consistent with the present results for other temperatures. Considering separately the rates of addition of free bromine and of tribromide ion, the same sequence is maintained, k_1 being, in each case, considerably higher than k_1'. Thus the effect of the methyl group in the α or β position is in the same direction and is more or less of a similar order of magnitude for the addition of both Br_2 and Br_3^-. This presumably indicates that essentially similar mechanisms operate in both the cases. As expected for an electrophilic reaction, the presence of a methyl group, on either of the ethylenic carbon atoms, facilitates the addition of bromine to the double bond, the methyl group in the α position being slightly more effective than in the β position.

Regarding relative reactivities of several substituted ethylenes, the results of Bell and his coworkers[3,4] show approximate agreement with what is to be expected from the known electron-withdrawing effects of the substituents. The present investigation includes a new type of compound, acrylamide. The rate of bromine addition to acrylamide is much faster than to acrylic ester. The internal mesomeric effect within the amide or ester group should result in a lower over-all electron-withdrawing effect on the part of the amide compared with the acrylic ester. Thus, it fits in with the accepted ideas that electrophilic bromine addition should be faster with acrylamide.

The energy of activation (E) for the addition of free bromine to the three esters studied lies in the order methacrylic < crotonic < acrylic. The order is what is to be expected from the known electron-releasing

TABLE II

RATE CONSTANTS FOR BROMINATION OF OLEFINS

k_1 = second-order rate constant for addition of Br_2
k_1' = second-order rate constant for addition of Br_3^-

Olefin	k_1, l. mol^{-1} sec^{-1}			k_1' l. mol^{-1} sec^{-1}			k_1'/k_1		
	20°	30°	40°	20°	30°	40°	20°	30°	40°
Acrylamide	0.72	1.62	3.58	0.18	0.48	1.08	0.25	0.30	0.30
Methyl acrylate	0.04	0.115	0.35	0.026	0.053	0.102	0.64	0.47	0.29
Methyl crotonate	1.00	2.72	6.20	0.42	0.82	1.53	0.42	0.30	0.25
Methyl methacrylate	2.30	5.24	9.20	0.95	2.04	3.92	0.41	0.39	0.43

TABLE III

COMPARISON OF ACTIVATION ENERGY (E), FREQUENCY FACTOR (A), AND ENTROPY OF ACTIVATION ($\Delta S^{\pm}$)[a] FOR THE REACTION BETWEEN SUBSTITUTED OLEFINS AND BROMINE

Substituted olefins	For reaction with the species Br_2, *i.e.*, for the rate constant k_1			For reaction with the species Br_3^-, *i.e.*, for the rate constant k_1'		
	E, kcal mol^{-1}	A, l. mol^{-1} sec^{-1}	$\Delta S^{\pm}$, cal deg^{-1} mol^{-1}	E', kcal mol^{-1}	A' l./mol^{-1} sec^{-1}	$\Delta S^{\pm\prime}$ cal deg^{-1} mole^{-1}
Acrylamide	14.6	5.8×10^{10}	−11.3	16.2	2.4×10^{11}	−8.5
Methyl acrylate	19.4	1.2×10^{13}	−0.7	12.4	4.2×10^{7}	−25.7
Methyl crotonate	16.5	2.0×10^{12}	−4.3	11.7	2.2×10^{8}	−22.3
Methyl methacrylate	13.3	1.8×10^{10}	−13.7	13.0	5.0×10^{9}	−16.2

[a] $S^{\pm}$ values are reported for 30°.

property of the methyl group. In the addition process, the point of attack is the α-carbon atom, and hence we may reasonably expect the methyl group in the α position (in methacrylic ester) to exert a relatively stronger effect than in the β position (in crotonic ester) The frequency factors lie in the same order as that for the activation energy shown above.

Again, the energy of activation for addition of bromine to acrylamide is appreciably lower than that for the reaction with acrylic ester. This is also in conformity with the relatively smaller electron-withdrawing effect of the amide group, compared with that of the ester group. The frequency factor is, however, much smaller for the amide, leading to a relatively high negative value for the entropy of activation.

Coming to the case of Br_3^- addition, the energy of activation (E') lies in the order crotonic < acrylic < methacrylic. The differences in the values of activation energy are, however, much less pronounced than for molecular bromine addition, and the data may not be accurate enough to justify any detailed discussion on the basis of such small differences. The frequency factors, which lie in the order acrylic > crotonic > methacrylic, are relatively low, the entropy of activation having a large negative value in each case.

The energy of activation for acrylic amide is appreciably higher than for the acrylic ester. For an electrophilic reaction, the reverse should be anticipated. The frequency factor, on the other hand, is much higher for the amide. It is difficult to correlate the results in terms of simple structural considerations.

Registry No.—Bromine, 7726-95-6; acrylamide, 79-06-1; methyl acrylate, 96-33-3; methyl crotonate, 623-43-8; methyl methacrylate, 80-62-6.

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