[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

The Kinetics of the Addition of Bromine to Some Cyclopropanes in Aqueous Acetic Acid

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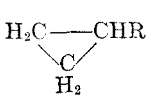
The rates of addition of bromine to a homologous series of cyclopropane carboxylic acids (Ia,b,c,d,e) and butylcyclopropane (If) have been studied in aqueous acetic acid. The second order rate constants obtained rise to a limiting value as the series is ascended. A mechanism involving electrophilic attack by bromine molecules as the rate-determining stage is suggested. Energies and entropies of activation are calculated for each member of the series.

Cyclopropanes are known to combine additively with bromine by fission of the cyclopropane ring.[2,3,4]

We now wish to report on the kinetics of this reaction in aqueous acetic acid solution. A series of homologous cyclopropane carboxylic acids (Ia,b, c,d,e) and the parent hydrocarbon butylcyclopropane (If) were chosen for study.



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(a) R = COOH
(b) R = CH_2COOH
(c) R = CH_2CH_2COOH
(d) R = $CH_2CH_2CH_2COOH$
(e) R = $CH_2CH_2CH_2CH_2COOH$
(f) R = $CH_2CH_2CH_2CH_3$

Cyclopropanecarboxylic acid (Ia) showed no tendency to absorb bromine from aqueous acetic acid solutions. This is in accordance with an earlier observation of Perkin.[5] The homologous cyclopropanes (Ib, c,d,e,f), however, absorbed one mole of bromine slowly under similar conditions. Rate measurements, carried out at varied dilutions and temperatures (Tables I, II, III, IV, V), gave consistent second-order rate constants (k_2) for the simple addition reaction:

$$\underset{II}{Br_2} + \underset{III}{\text{cyclopropane}} \longrightarrow \underset{IV}{[Br_2, \text{cyclopropane}]} \longrightarrow \text{Fission Products}$$

TABLE I

SECOND ORDER RATE CONSTANTS FOR THE ADDITION OF BROMINE TO CYCLOPROPANEACETIC ACID IN 37.5% AQUEOUS ACETIC ACID (concentrations M/20)

Temp., °C.	Absorption of Bromine, %	Time (min.)	10^6k_2 (sec.$^{-1}$)
0	2.7	2820	3.27
	5.9	7020	2.98
		k_2(mean) = 3.12×10^{-6}	
24	8.0	1200	24.2
	13.4	2070	24.7
	18.0	2820	25.9
		k_2(mean) = 24.9×10^{-6}	
40	4.5	135	116
	14.0	495	110
	27.0	1325	93
		k_2(mean) = 106×10^{-6}	

TABLE II

SECOND ORDER RATE CONSTANTS FOR THE ADDITION OF BROMINE TO CYCLOPROPANEPROPIONIC ACID IN 37.5% AQUEOUS ACETIC ACID (concentrations M/20)

Temp., °C.	Absorption of Bromine, %	Time (min.)	10^5k_2 (sec.$^{-1}$)
0	5.5	330	6.26
	9.5	570	6.14
	13.5	810	6.42
		k_2(mean) = 6.27×10^{-5}	
24	20.0	120	69.4
	25.5	180	63.2
	30.5	240	61.0
		k_2(mean) = 64.5×10^{-5}	
40	18.0	40	183
	28.0	70	185
	41.0	130	179*
		k_2(mean) = 184×10^{-5}	

* k_2 values above 40% absorption of bromine not included in mean value.

TABLE III

SECOND ORDER RATE CONSTANTS FOR THE ADDITION OF BROMINE TO CYCLOPROPANEBUTYRIC ACID IN 37.5% AQUEOUS ACETIC ACID (concentrations M/80)

Temp., °C.	Absorption of Bromine, %	Time (min.)	10^5k_2 (sec.$^{-1}$)
0	6.0	300	28.4
	8.0	420	27.6
	11.0	600	27.5
		k_2(mean) = 27.8×10^{-5}	
24	13.0	60	332
	18.5	90	336
	23.5	130	315
		k_2(mean) = 328×10^{-5}	
40	11.2	20	841
	17.8	30	962
	26.5	50	960
		k_2(mean) = 921×10^{-5}	

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[1] Visiting Postdoctoral Fellow, Princeton University, 1953–1954. Present address, Department of Chemistry, Birmingham University, England.

[2] Wagner, Wolff, and Wallis, *J. Org. Chem.*, **17**, 529 (1952).

[3] Kharasch, Fineman, and Mayo, *J. Am. Chem. Soc.*, **61**, 2139 (1939).

[4] Vogel, *Fortschritte der Chemischen Forschung*, **3**, 472 (1955).

[5] Perkin, *J. Chem. Soc.*, **47**, 816 (1885).

TABLE IV

SECOND ORDER RATE CONSTANTS FOR THE ADDITION OF BROMINE TO CYCLOPROPANEVALERIC ACID IN 37.5% ACETIC ACID (concentrations M/40)

Temp., °C.	Absorption of Bromine, %	Time (min.)	10^4k_2 (sec.$^{-1}$)
0	30	450	6.36
	34.5	630	5.58
		k_2(mean) = 5.97×10^{-4}	
24	26	40	58.6
	38	80	51.1
	50	140	47.6*
		k_2(mean) = 54.8×10^{-4}	
40	21.5	20	177
	27.5	30	169
	38.5	50	167
		k_2(mean) = 171×10^{-4}	

* k_2 values above 40% absorption of bromine not included in mean value.

TABLE V

SECOND ORDER RATE CONSTANTS FOR THE ADDITION OF BROMINE TO BUTYLCYCLOPROPANE IN 37.5% AQUEOUS ACETIC ACID (concentrations M/80)

Temp., °C.	Absorption of Bromine, %	Time (min.)	10^4k_2 (sec.$^{-1}$)
0	15.5	180	13.6
	21.5	300	12.2
	31.5	480	12.8
		k_2(mean) = 12.9×10^{-4}	
24	16.0	20	127
	21.0	30	118
	30.5	50	117
		k_2(mean) = 121×10^{-4}	
40	12.5	5	382*
	29.5	15	371
	40.0	25	355
		k_2(mean) = 363×10^{-4}	

* k_2 values measured at less than ten minutes not included in mean value.

Plots of $-\log k_2$ against the number of carbon atoms (n) intervening between the cyclopropane ring and the carboxyl group (Figure 1) show that $-\log k_2$ decreases to a limiting value as n increases along the homologous series. The limiting value corresponds to $-\log k_2$ for butylcyclopropane (if, $n = \infty$) where the carboxyl group is at an infinite distance from the ring.

The influence of temperature on the rates of addition is expressed by Arrhenius plots (Figure 2) corresponding to an energy of activation ($E_{exp.} = 14.5 \pm 1$ kcal.) which is constant within experimental error for each member of the series (Table VI). The entropies of activation ($\Delta S_c^\ddagger$, n = 1, 2, 3, 4) were calculated from the absolute rate equation:[6]

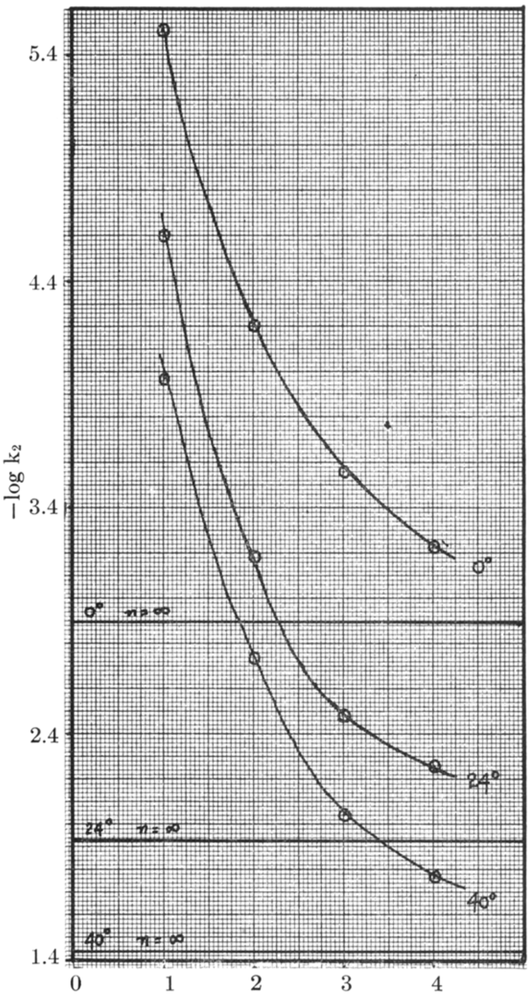

FIG. 1.—CHANGE OF SECOND-ORDER RATE CONSTANTS (k_2) WITH NUMBER OF CARBON ATOMS (n) BETWEEN CYCLOPROPANE RING AND CARBOXYL GROUP.

$$k = e\frac{kT}{h}\, e^{-E_{exp.}/RT}\, e^{\Delta S_c^\ddagger/R}$$

by substituting $E_{exp.} = 14.5$ kcal., and the corresponding constants (k_2, n = 1, 2, 3, 4) for any one temperature (Table VI). The values of $\Delta S_c^\ddagger$ plotted against n (Figure 3) lie on a smooth curve which approaches the limiting value of $\Delta S_c^\ddagger$ for butylcyclopropane.

Our general reaction follows similar kinetics to the addition of bromine to olefines in aqueous acetic acid.[7,8,9] This suggests a common mechanism involving electrophilic attack by bromine molecules as the rate-determining stage. We postulate an intermediate activated complex (IV) which arises by co-ordination of the positive center in a polarized bromine molecule with the delocalized orbitals of

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(6) Glasstone, Laidler, and Eyring, *The Theory of Rate Processes*, McGraw-Hill Book Co., New York, 1941, p. 199.

(7) Robertson, Clare, McNaught, and Paul, *J. Chem. Soc.*, 335 (1937).

(8) Evans, Watson and Robertson, *J. Chem. Soc.*, 1624 (1950).

(9) De la Mare, *Quart. Revs.* (*London*), **3**, 126 (1949).

TABLE VI

MEAN SECOND ORDER RATE CONSTANTS, ENERGIES, AND ENTROPIES OF ACTIVATION FOR THE ADDITION OF BROMINE TO HOMOLOGOUS CYCLOPROPANES

Cyclopropane derivative	$k_2(0°)$	$k_2(24°)$	$k_2(40°)$	$\log k_2$ (0°)	$\log k_2$ (24°)	$\log k_2$ (40°)	$E_{exp.}$ (kcal.)	$-\Delta S_0^{\ddagger}$ (e.v.)
Cyclopropaneacetic acid	3.12×10^{-6}	24.9×10^{-6}	106×10^{-6}	−5.51	−4.60	−3.97	15.1	32.6
Cyclopropanepropionic acid	6.27×10^{-5}	64.5×10^{-5}	184×10^{-5}	−4.20	−3.18	−2.74	14.2	26.6
Cyclopropanebutyric acid	27.8×10^{-5}	328×10^{-5}	921×10^{-5}	−3.56	−2.48	−2.04	15.0	23.4
Cyclopropanevaleric acid	5.97×10^{-4}	54.8×10^{-4}	171×10^{-4}	−3.22	−2.26	−1.77	14.2	21.8
Butylcyclopropane	12.9×10^{-4}	121×10^{-4}	363×10^{-4}	−2.89	−1.92	−1.44	14.1	20.6
			$E_{exp.}$ (mean) = 14.5					

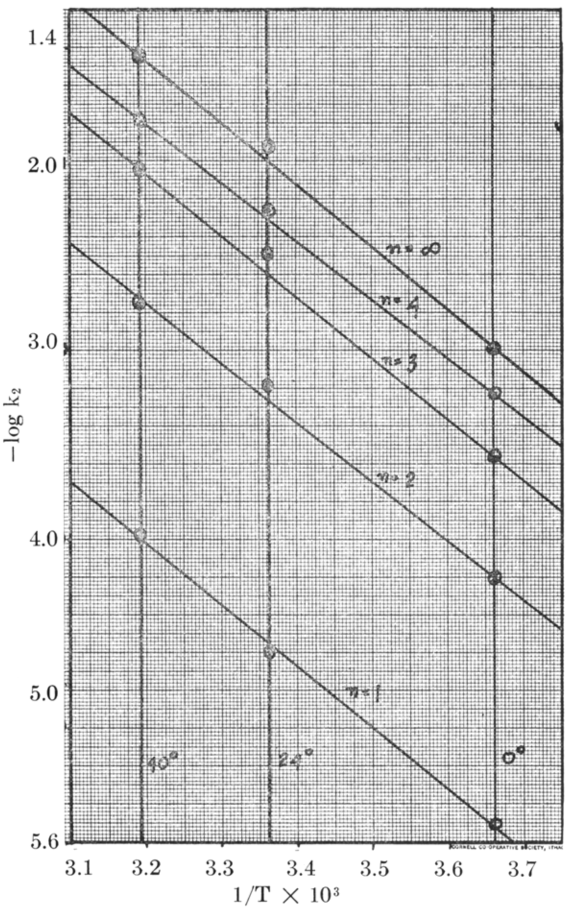

FIG. 2.—CHANGE OF SECOND-ORDER RATE CONSTANTS (K_2) WITH TEMPERATURE.

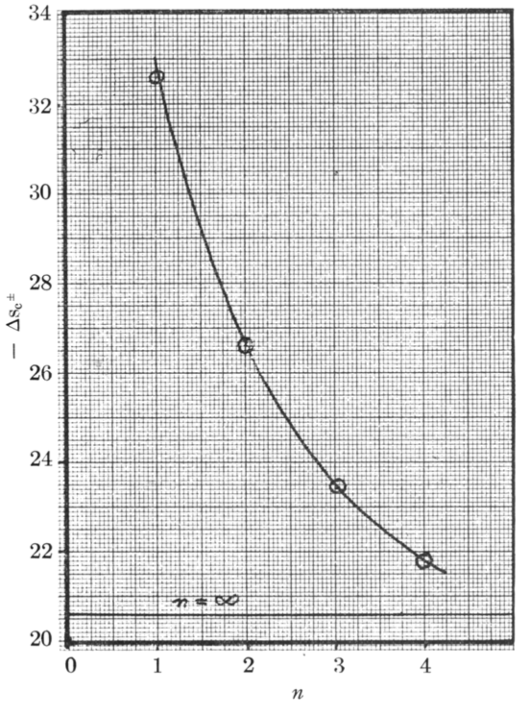

FIG. 3.—CHANGE OF ENTROPIES OF ACTIVATION ($S_e^{\ddagger}$) WITH NUMBER OF CARBON ATOMS (n) BETWEEN CYCLOPROPANE RING AND CARBOXYL GROUP.

the cyclopropane ring,[4,10] fission of which completes the reaction. The addition of bromine to olefins may involve a similar intermediate complex of the π-bonded type.[9,11] This mechanism is in agreement with our observation that the rate of addition of bromine is decreased by added bromide ion (lithium bromide) which reduces the concentration of bromine molecules[7,8] by the equilibrium:

$$Br_2 + Br^{\ominus} \rightleftharpoons Br_3^{\ominus}$$

The influence of the carboxyl group is also consistent. The inertness of cyclopropanecarboxylic acid (Ia) to the addition of bromine in our experiments[12] we ascribe to conjugation between the cyclopropane ring and the adjacent carboxyl group[4] which reduces the availability of the cyclopropane orbitals for coordination with electrophilic bromine. The anomalously slow bromination of acrylic acid in acetic acid solution[7] is analogous. In cyclopropaneacetic acid (Ib) where conjugation is not involved, the orbitals of the cyclopropane ring are restrained by the inductive effect (−I) of the car-

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(10) Tipper, *J. Chem. Soc.*, 713, 2045 (1955).

(11) Dewar, *Ann. Repts. Progr. Chem.* (*Chem. Soc. London*), **48,** 117 (1951).

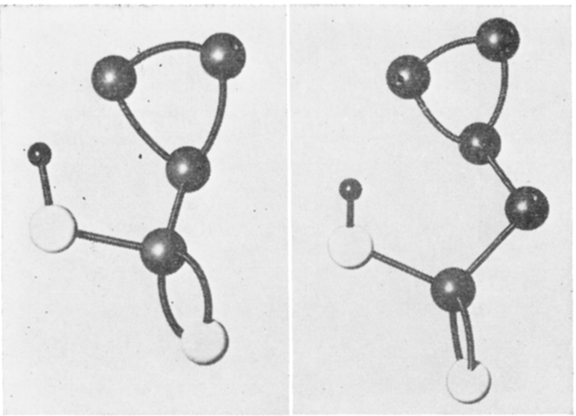
(12) Cyclopropanecarboxylic acid in carbon tetrachloride slowly absorbs bromine on irradiation. A radical mechanism may be involved in this, and similar cases.[3,13]

(13) Kishner, *Chem. Zentr.*, **II,** 1130 (1909).

boxyl group. Consequently bromine is bonded only weakly, and the rate of addition is slow.[14] As the series of homologous acids is ascended (Ic,d,e) the cyclopropane orbitals grow less restrained as the inductive effect weakens, and the rate of addition of bromine increases. A limiting rate is reached in the case of butylcyclopropane (If) where the inductive effect of the carboxyl group no longer operates.

In the light of recent work[15] the inductive effect observed may be ascribed primarily to spatial interaction between the carboxyl group and the cyclopropane ring.[10]

Hydrogen bonded structures such as would reduce the availability of the cyclopropane orbitals for coordination with bromine. The effect would decrease on ascending the series due to weakening of the hydrogen bonding in the larger ring structures.



Photograph of Cyclopropanecarboxylic Acid Model (*left*), and Cyclopropaneacetic Acid Model (*right*), Showing Possibility for Hydrogen Bonding Between Carboxylic Hydrogen and the Cyclopropane Ring.

The negative values of $\Delta S_c^\ddagger$, which suggest an ordered, solvated activated complex, account for the fact that addition of bromine is slow despite the low value of the activation energies. Since the latter are constant the increase in reaction rate along the series is determined largely by the increase in $\Delta S_c^\ddagger$ due to a loosening of the complex as a whole, and a breaking down of solvation.

EXPERIMENTAL

Cyclopropanecarboxylic acid (Ia). The acid, prepared by the methods of McCloskey and Coleman,[16] and Smith and McKenzie,[17] was obtained as a colorless liquid (b.p. 80–82°, 15 mm.).

Calc'd, equivalent for $C_4H_6O_2$: 86.1. Found, equivalent: 86.6.

Cyclopropaneacetic acid (Ib). Cyclopropanecarboxylic acid (25 g.) was cooled in ice and thionyl chloride (42 g.) was dropped in. The product was warmed on a steam-bath for one hour, dissolved in dry ether (100 cc.), and dropped into a well-stirred solution of diazomethane (35 g.) in ether (1200 cc.). The mixture was set aside at room temperature for one day, and the ether was removed, leaving the diazoketone which was dissolved in methanol (50 cc.), and dropped into a suspension of silver oxide (1.0 g.) in boiling methanol (175 cc.). Further portions of silver oxide (8 g.) were added at intervals to the refluxing mixture, until a test portion no longer evolved nitrogen on acidifying with hydrochloric acid. The mixture was filtered, basified with aqueous potassium hydroxide (2.5 *N*, 250 cc.), refluxed for two hours, and the excess methanol was distilled off. The mixture was cooled, extracted with ether, and the aqueous layer was acidified (Congo) with ice-cold sulfuric acid (2.5 *N*). Cyclopropaneacetic acid separated as an oil which was isolated by extraction with ether and distilled under reduced pressure as a colorless liquid (13.5 g., 47%) boiling at 90°/15 mm. Smith and McKenzie[17] reported b.p. 189–191°/750 mm.

Calc'd, equivalent for $C_5H_8O_2$: 100.1. Found, equivalent: 100.4.

The *p-bromophenacyl ester*, prepared in the usual way, and crystallized from petroleum ether, melted at 82°; Smith and McKenzie reported m.p. 83°.

Cyclopropanepropionic acid (Ic). The acid, prepared from cyclopropaneacetic acid by the foregoing procedure, was obtained as a colorless liquid b.p. 101°/15 mm.

Calc'd, equivalent for $C_6H_{10}O_2$: 114. Found, equivalent: 113.

Anal. Calc'd for $C_6H_{10}O_2$: C, 63.10; H, 8.83. Found: C, 62.81; H, 8.97.

Cyclopropanebutyric acid (Id). The acid, prepared from cyclopropanepropionic acid, was obtained as a colorless liquid b.p. 115°/15 mm.

Calc'd, equivalent for $C_7H_{12}O_2$: 128. Found, equivalent: 127.

Anal. Calc'd for $C_7H_{12}O_2$: C, 65.60; H, 9.44. Found: C, 65.13; H, 9.16.

Cyclopropanevaleric acid (Ie). The acid, prepared from cyclopropanebutyric acid, was obtained as a colorless liquid b.p. 127°/15 mm.

Calc'd, equivalent for $C_8H_{14}O_2$: 140. Found, equivalent: 142.

Anal. Calc'd for $C_8H_{14}O_2$: C, 67.56; H, 9.93. Found: C, 66.90; H, 9.43.

Butylcyclopropane (If). The hydrocarbon, prepared by the Gustavson cyclization of 2-butyl-1,3-dibromopropane according to the procedure of Pines, Huntsman, and Ipatieff,[18] was obtained as a colorless liquid b.p. 97–99°.

Anal. Calc'd for C_7H_{14}: C, 85.62; H, 14.39. Found: C, 86.11; H, 14.70.

Rate studies of the addition of bromine in aqueous acetic acid. Acetic acid (duPont, C.P. Reagent) was purified by freezing and fractional distillation over chromium trioxide. *Bromine* was purified by distillation over potassium bromide. Reactions were carried out in stoppered, amber glass bottles immersed in a thermostat. Standard solutions of bromine and of each of the cyclopropanes in 37.5% aqueous acetic acid were freshly prepared. Accurately measured volumes of the reagent solutions were mixed at 0°, 24°, and 40° and the rate of bromination was followed by titration with standard sodium thiosulphate.

Acknowledgment. We wish to thank Merck and Co., Inc., Rahway, New Jersey, for a generous gift of α-acetyl-γ-butyrolactone.

Princeton, New Jersey

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[14] The rate of addition of bromine is increased by dilution with water. The effect may be attributed to increased polarization of bromine molecules by solvation[7,8] and ionization of the carboxyl group (-I decreases).

[15] Grob, Renk, and Kaiser, *Chemistry & Industry*, 1222 (1955).

[16] McCloskey and Coleman, *Org. Syntheses*, **24**, 36 (1944), John Wiley and Sons, Inc., New York.

[17] Smith and McKenzie, *J. Org. Chem.*, **15**, 74 (1950).

[18] Pines, Huntsman, and Ipatieff, *J. Am. Chem. Soc.*, **75**, 2315 (1953).