much smaller than the corresponding heat for wüstite. At the same temperature for the reaction $2Fe_3O_4$ (mag.) + $^1/_2O_2(g) \rightarrow 3Fe_2O_3$ (hem.), ΔH is $-54{,}500$.

By evaporation of iron oxide in a vacuum furnace at 1600° it was found that the total vapor pressure passes through a minimum at an atomic ratio of O:Fe = 1.116 (24.23% oxygen). From this composition of the azeotropic mixture it is calculated that the vapor pressure of liquid iron at 1600° is 5.8×10^{-5} atm. and it is shown that the vapor pressure of molecular FeO is small in comparison thereto.

KEARNY, N. J. RECEIVED NOVEMBER 14, 1945

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, POLYTECHNIC INSTITUTE OF BROOKLYN]

The Kinetics of the Reaction of Sodium 2-Haloethanesulfonates with Aqueous Alkali

BY E. F. LANDAU,[1] W. F. WHITMORE AND PAUL DOTY

The kinetics of the reactions of various alkyl halides with hydroxide ion[2] has been the subject of intensive and fruitful investigation, especially by the Hughes–Ingold group, for more than a decade. These researches demonstrated that in some cases the reaction proceeded to the alcohol (substitution) or to the olefin (elimination), but more frequently to the simultaneous occurrence of both types with the substitution reaction predominating. Moreover, two different mechanisms are possible for each of the above categories; one is monomolecular, the other bimolecular.

The two nucleophilic substitution mechanisms are

$$
\begin{array}{ll}
S_n1 & RX \longrightarrow R^+ + X^- \text{ (slow)} \\
 & R^+ + OH^- \longrightarrow ROH \text{ (fast)} \\
S_n2 & OH^- + RX \longrightarrow ROH + X^-
\end{array}
$$

These reactions differ fundamentally only in the degree of the solvolytic ionization whose predominance is responsible for the S_n1 reaction. It has been shown that a decrease in the electronegativity of the alkyl group favors the ionization and increases the speed of the S_n1 reaction. In the S_n2 reaction the higher the electronegativity of the alkyl group the faster the reaction should be because of the increased tendency of the alkyl group to share the electrons of the hydroxide group. This situation has been illustrated by Gleave, Hughes and Ingold[3] and others[4] by showing that in the series—methyl, ethyl, isopropyl, *t*-butyl iodide—the S_n2 reaction predominated for the first two members while the S_n1 reaction is dominant for the latter two iodides.

The elimination reactions which frequently accompany these substitution reactions have the form[5]

$$OH^- + HCR_2CR_2X \longrightarrow H_2O + R_2C{=}CR_2 + X^-$$

A monomolecular reaction (E1) would be expected from an electrophilic attack by the solvent on X to form a carbonium ion. The hydroxide ion would then accept a proton in a fast reaction to give the olefin. A bimolecular reaction (E2) would conceivably result from a nucleophilic attack by the hydroxide ion on a β-hydrogen atom. The mechanism for this reaction will be discussed later. In the case of primary alkyl halides the elimination reactions studied have been of second order[6] while for halides containing secondary and tertiary halides the reactions are predominantly first order.[7,8,9,10,11]

Hughes and Shapiro[9] in their study of the mechanism of substitution at a saturated carbon atom have discovered that the two substitution reactions and the bimolecular elimination reaction have comparable velocities for the case of the isopropyl halides in a water–alcohol medium. They have evaluated the A and E parameters in the Arrhenius equation and find that these quantities are only slightly dependent upon the particular halogen present. However, when the ethyl bromide reaction is studied[12] (in anhydrous alcohol) it is found that only the bimolecular reactions occur with the substitution reaction predominating to the extent of about 99%. On the other hand, *t*-butyl halides yield mostly isobutylene via a bimolecular reaction (E2) in anhydrous alcohol.

Thus, with the course of these alkyl halide reactions apparently so dependent upon the presence or absence of a relatively electropositive group on the β-carbon, it is of interest to record a kinetic study of the reaction in water medium of sodium 2-chloro- and 2-bromo-ethanesulfonate ($CH_2XCH_2SO_3Na$) with hydroxide ions.

Experimental

It has been reported elsewhere[13] that this reaction can be represented as

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[1] Taken in part from a thesis submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy, Polytechnic Institute of Brooklyn, 1945. Present Address: Celanese Corp., Newark, N. J.

[2] Remick, "Electronic Interpretations of Organic Chemistry," John Wiley and Sons, New York, N. Y., 1943.

[3] Gleave, Hughes and Ingold, *J. Chem. Soc.*, 236 (1935).

[4] Koskoski, Thomas and Fowler, THIS JOURNAL, **63**, 2451 (1941).

[5] Hanhart and Ingold, *J. Chem. Soc.*, 997 (1927).

[6] Hughes and Shapiro, *ibid.*, 1177 (1937).

[7] Hughes, Ingold and Scott, *ibid.*, 1271 (1937).

[8] Bodendorf and Bohme, *Ann.*, **516**, 1 (1935).

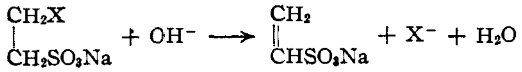
[9] Hughes and Shapiro, *J. Chem. Soc.*, 1192 (1937).

[10] Cooper, Hughes and Ingold, *ibid.*, 1280 (1937).

[11] Hughes and McNulty, *ibid.*, 1283 (1937).

[12] Grant and Hinshelwood, *ibid.*, 258 (1933).

[13] E. F. Landau, Thesis, Polytechnic Institute of Brooklyn, 1945.



$$\begin{matrix} CH_2X \\ | \\ CH_2SO_3Na \end{matrix} + OH^- \longrightarrow \begin{matrix} CH_2 \\ \| \\ CHSO_3Na \end{matrix} + X^- + H_2O$$

and that yields of purified sodium vinylsulfonate in excess of 60% are obtained. Preliminary experiments showed that conversion could be followed readily by observing the disappearance of the alkali and that the reaction was of approximately second order with a half life of about three hours at room temperature.

In the experimental work which then followed, 50 ml. of a solution of standard sodium hydroxide was mixed with an equal volume of a solution of equivalent concentration of purified sodium 2-chloroethanesulfonate and the temperature of the reaction mixture was held constant to 0.1° in a thermostat. The rate was followed by withdrawing aliquot samples of the solution at recorded time intervals. These aliquot samples were added to aqueous standard acid which stopped the reaction. Back titration with standard alkali permitted the calculation of the extent of reaction at that time.

Tables I, II and III summarize the results of these experiments at 25.0, 9.5 and 1°.

TABLE I

DECOMPOSITION OF 2-CHLOROETHANESULFONATE AT 25°

a = concentration of NaOH = 0.458 mole/liter; b = concentration of $ClCH_2CH_2SO_3Na$ = 0.458 mole/liter = a

Time, sec. $\times 10^{-3}$	x, moles/liter	k, liters/mole sec.	Time, sec. $\times 10^{-3}$	x, moles/liter	k, liters/mole sec.
0	0	..	3.00	0.112	24.4
0.337	0.017	24.9×10^{-5}	3.64	.132	23.6
.517	.025	24.4	4.52	.151	24.3
.752	.035	24.0	5.44	.168	23.8
1.10	.051	24.0	6.36	.186	23.5
1.52	.006	24.7	7.49	.200	22.7
1.82	.078	24.3			Av. = 24.2 ±
2.40	.097	24.2			0.7×10^{-5}

TABLE II

DECOMPOSITION OF 2-CHLOROETHANESULFONATE AT 9.5°

a = concn. of NaOH = 0.446 mole/liter; b = concn. of $ClCH_2CH_2SO_3Na$ = 0.446 mole/liter = a

Time, sec. $\times 10^{-4}$	x, moles/liter	k, liters/mole sec.
0	0	..
0.270	0.0257	5.08×10^{-5}
.570	.0474	4.67
.916	.0684	4.36
1.44	.0969	4.32
1.98	.122	4.27
2.38	.137	4.18
2.79	.153	4.19
		Av. = $4.44 \pm 0.25 \times 10^{-5}$

TABLE III

DECOMPOSITION OF 2-CHLOROETHANESULFONATE AT 1.0°

a = concentration of NaOH = 0.428 mole/liter; b = concentration of $ClCH_2CH_2SO_3Na$ = 0.428 mole/liter = a

Time, sec. $\times 10^{-4}$	x, moles/liter	k, liters/mole sec.
0	0	..
0.370	0.0118	1.79×10^{-3}
0.760	.0247	1.88
1.25	.0385	1.84
1.92	.0524	1.70
2.16	.0583	1.70
3.22	.0850	1.79
3.79	.0999	1.98
8.22	.162	1.73
		Av. = $1.79 \pm 0.06 \times 10^{-5}$

The specific reaction rate was also determined graphically by plotting $1/(a - x)$ against time. The values obtained by the graphical method and by calculation compare favorably. These are recorded together with the half-life in Table IV.

TABLE IV

RATE CONSTANT AND HALF-LIFE OF DECOMPOSITION OF SODIUM 2-CHLOROETHANESULFONATE

Temp., °C.	k (graph)	k, liters/mole sec.	Half-life, sec.
25	23.2×10^{-5}	24.2×10^{-5}	9,030
9.5	4.31	4.44	55,600
1.1	1.74	1.79	131,000

As a further verification of the order of reaction a determination of the rate was made with unequal initial concentrations of reactants. The results of this experiment are tabulated in Table V.

TABLE V

DECOMPOSITION OF SODIUM 2-CHLOROETHANESULFONATE AT 25°

a = concn. of NaOH = 0.538 mole/liter; b = concn. of $ClCH_2CH_2SO_3Na$ = 0.358 mole/liter

Time, sec. $\times 10^{-4}$	x, moles/liter	$\log \frac{b(a-x)}{a(b-x)}$	k, l/mole/sec.
0	0	0	..
0.09	0.035	0.0158	19.8×10^{-5}
.27	.096	.0512	24.3
.51	.151	.0949	23.8
1.17	.234	.2122	23.2
1.59	.262	.2817	22.7
1.938	.277	.3310	21.9
2.286	.293	.2817	22.4
			Av. = $23.1 \pm 0.07 \times 10^{-5}$

TABLE VI

DECOMPOSITION OF $BrCH_2CH_2SO_3Na$ AT 25°

a = concn. of NaOH = 0.461 mole/liter; b = concn. of $BrCH_2CH_2SO_3Na$ = 0.461 mole/liter = a

Time, sec. $\times 10^{-3}$	x, moles/liter	k, liters/mole sec.
0	0	
0.360	0.096	158×10^{-5}
.600	.140	157
.960	.190	159
1.38	.230	156
1.86	.261	152
2.50	.293	147
3.60	.322	139
		Av. = $149 \pm 7 \times 10^{-5}$

The slope of the line obtained by plotting the log $b(a - x)/a(b - x)$ against t is equal to 0.182×10^{-4}; by multiplying this value by $2.303/(a - b)$ a value of k equal to 23.3×10^{-5} liter/mole second is obtained. Thus, the value of the specific reaction rate obtained in this experiment compared favorably with the value of k obtained when the initial concentrations of a and b were equal.

The evaluation of the rate constants for the conversion

TABLE VII

DECOMPOSITION OF $BrCH_2CH_2SO_3Na$ AT 12°

a = concn. NaOH = 0.423 mole/liter; b = concn. of $BrCH_2CH_2SO_3Na$ = 0.423 mole/liter = a

Time, sec. $\times 10^{-4}$	x, moles/liter	k, liters/mole sec.
0	0	..
0.060	0.040	41.1×10^{-5}
.15	.086	40.2
.27	.133	40.2
.45	.179	38.5
.97	.253	36.2
.99	.256	36.6
1.26	.276	35.2
1.47	.291	35.4
		Av. = $37.9 \pm 2.1 \times 10^{-5}$

TABLE VIII

DECOMPOSITION OF $BrCH_2CH_2SO_3Na$ AT 1°

a = concn. of NaOH = 0.454 mole/liter; b = concn of $BrCH_2CH_2SO_3Na$ = 0.454 mole/liter = a

Time, sec. $\times 10^{-4}$	x, moles/liter	k, liters/mole sec.
0	0	.
0.060	0.0148	12.4×10^{-5}
.186	.0422	12.1
.396	.0809	12.1
.606	.111	11.8
.786	.133	11.6
1.28	.189	12.2
1.67	.212	11.6
2.60	.255	10.9
		Av. = $11.8 \pm 4 \times 10^{-5}$

of sodium 2-bromoethanesulfonate at several temperatures was performed under experimental conditions similar to those employed in the study of the corresponding chloro compound. These results are summarized in Tables VI, VII and VIII.

The values of k obtained by plotting $1/(a - x)$ against time compare favorably with the values obtained by calculation as shown in Table IX.

TABLE IX

RATE CONSTANTS FOR THE DECOMPOSITION OF SODIUM 2-BROMOETHANESULFONATE

Temp., °C.	k (calculated)	k (graph)
25	149×10^{-5}	140×10^{-5}
12	37.9	35.3
1.1	11.8	11.5

Discussion

The logarithm of the rate constant is plotted as a function of reciprocal absolute temperature in Fig. 1 for these two reactions. From the slope of these straight lines one obtains a value of 17.4 ± 0.2 kcal. per mole for the activation energy of each reaction. The frequency factor in the Arrhenius equation is then easily calculated from the rate constants and found to be 1.26×10^9 for the chloro compound and 7.8×10^9 for the bromo compound.

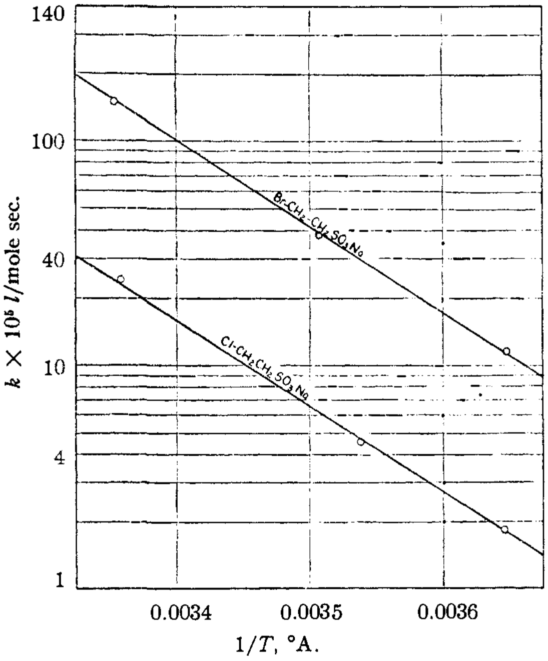


Fig. 1.—Plot of logarithm of reaction rate constant versus reciprocal of absolute temperature for the decomposition of sodium 2-chloro- and bromoethanesulfonate.

It is instructive to compare these figures with corresponding quantities determined in a study of the bimolecular reaction of hydroxide ions with ethyl halides in anhydrous alcohol[12] and with isopropyl halides in alcohol–water medium.[7] Unfortunately, the solvent medium varies in this comparison and consequently only large differences should be considered significant. In each case the data correspond to the sum of the bimolecular substitution and elimination reactions. The substitution reaction predominates for the ethyl halides, whereas the elimination reaction predominates in the other cases. The frequency factors, the energies of activation and the rate constants at 80° are compared in Table X.

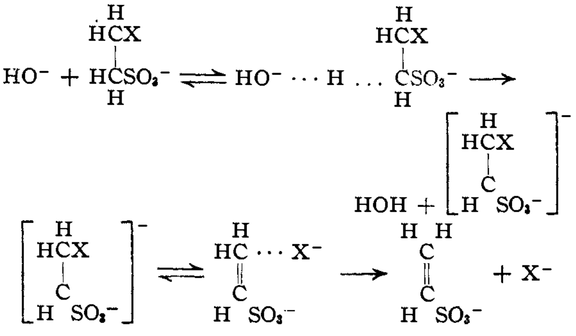
TABLE X

COMPARISON OF KINETIC CONSTANTS FOR THE BIMOLECULAR REACTIONS OF HYDROXIDE IONS AND ALKYL HALIDES

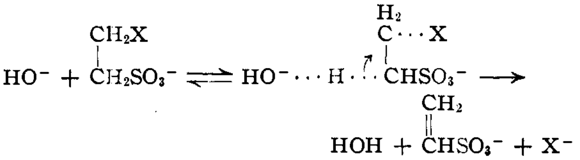
	C_2H_5X in anhyd. ethyl alcohol	$(CH_3)_2CHX$ 60% alc.–water	$(CH_3)_2CHX$ 80% alc.–water	CH_2X–$CH_2SO_3^-$ in water
	Energy of activation (kcal.)			
Cl	23.0	....	24.0	17.4
Br	21.0	21.6	22.2	17.4
I	21.0	21.8	....	....
	Frequency factor $\times 10^9$			
Cl	149	....	29.0	1.26
Br	241	15.7	56.2	7.8
I	508	105.5	....	....
	Rate constant at 80°C. $\times 10^4$			
Cl	7.73	....	0.325	252
Br	226	8.57	12.8	1560
I	460	31.3	....	....

An examination of this table and the previous kinetic data indicate that the following points deserve explanation by any mechanism that is postulated. 1, An elimination reaction predominates. 2, It is a bimolecular reaction. 3, The energies of activation for the 2-haloethanesulfonates are smaller than for the other reactions and are independent of the halogen present. 4, The frequency factors are smaller and depend more on the particular halogen present than in the other cases presented.

A nucleophilic attack by a hydroxide ion on a β-hydrogen to produce the carbanion which then undergoes solvolytic ionization of the halide atom is a mechanism which is consistant with all the above noted considerations. Schematically this would take the form



The sulfonate group attracts electrons from the carbon–hydrogen bonds attached to the carbon 1 and produces at this carbon and the hydrogen attached to it the most electrophilic point in the molecule. Hydroxide ions are attracted to this point and form the transition state by attracting an already activated hydrogen. In the next step the electron pair partially released in the first step shifts toward the other carbon (now most electrophilic) permitting the solvolytic ionization of the halogen and the formation of the olefin. The first reaction is rate controlling and is responsible for the measured energy of activation. This formulation is at present probably indistinguishable from the postulation that only one transition state is involved as shown.



$$\mathrm{HO^- + \overset{CH_2X}{\underset{CH_2SO_3^-}{|}} \rightleftharpoons HO^-\cdots H\cdots \overset{\overset{H_2}{C}\cdots X}{\underset{CHSO_3^-}{|}} \longrightarrow HOH + \overset{CH_2}{\underset{CHSO_3^-}{\|}} + X^-}$$

However, the complete independence of the energy of activation on the halogen present would seem to exclude the activation of the carbon–X bond in the transition state complex.

It is obvious that either variation of this mechanism would account for a bimolecular elimination reaction (points 1 and 2). Point 3 is explained, as already indicated, by the negative inductive effect of the sulfonate ion which facilitates the release of the proton to the hydroxide ion. It appears that this step which consumes all the energy of activation is consequently independent of the halogen present on the other carbon. The lower frequency factors (point 4) here observed would be expected if it were necessary for the transition state to be in a *trans* configuration as shown, for steric hindrance would make such a configuration less probable than in the other cases. Moreover, the greater attraction (inductive field effect) of bromine than chlorine for the sulfonate group may be responsible for the more frequent occurrence of the *trans* configuration in the bromo compound and hence the larger frequency factor.

Acknowledgment.—We wish to thank the Armstrong Cork Company of Lancaster, Pa., for their support in the investigation, and Dr. P. O. Powers and Professor C. C. Price for their helpful suggestions.

Summary

Rate measurements on the reaction of sodium 2-haloethanesulfonates with hydroxide ions in water medium at several temperatures show the reaction to be second order. The rate constants are given by the expressions:

$$k_{\mathrm{Cl}} = 1.26 \times 10^9 e^{-17400/RT}$$
$$k_{\mathrm{Br}} = 7.8 \times 10^9 e^{-17400/RT}$$

The nucleophilic elimination mechanism postulated accounts for the observed features of the reaction and the major differences between these reactions and the corresponding reactions of some alkyl halides.

RECEIVED NOVEMBER 23, 1945

[CONTRIBUTION FROM THE DEPARTMENT OF PHYSIOLOGICAL CHEMISTRY, THE JOHNS HOPKINS UNIVERSITY]

Aliphatic Diazo Compounds.[1] Investigation of α-Diazo-γ,γ,γ-triphenylpropane, in Relation to Molecular Rearrangements and Stability[2]

BY LESLIE HELLERMAN AND R. L. GARNER

Our interest in the aliphatic diazo series, and particularly the phenylated derivatives such as diazo-β,β,β-triphenylethane and α-diazo-γ,γ,γ-triphenylpropane, has centered in problems concerned with the relationship of their structure to stability and their relative tendency to undergo intramolecular rearrangements, as well as with the bearing of their properties upon the mechanism of the action of nitrous acid upon primary amines[1a] and the amino acids. We have described[1c] the thermal rearrangement of diazo-β,β,β-triphenylethane, $(C_6H_5)_3CCH(N_2)$, to yield triphenylethylene as the major product, with triphenylacetaldazine in small amount; and, the conditions under which the decomposition of this diazo compound yields, in the presence of certain organic acids, esters related to benzyldiphenylcarbinol, and in the presence of nitrogen trioxide, triphenylnitroethylene. There has been discussed the theory of these actions, and it has been shown that the decomposition of the nitrite of β,β,β-triphenylethylamine, yields rearrangement products analogous to those obtained from the above-named diazo compound derived from this amine.

In contrast, it now is demonstrated that the homolog, α-diazo-γ,γ,γ-triphenylpropane, $(C_6H_5)_3CCH_2CH(N_2)$, generally possesses greater "stability" than the diazoethane, and indeed many of the diazoalkanes that have been described, and shows little tendency to undergo rearrangements under conditions that invariably promote such reactions in the case of the more

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[1] Antecedent papers in this series: (a) Hellerman, Cohn and Hoen, THIS JOURNAL, **50**, 1716–1729 (1928); (b) Hellerman and Newman, *ibid.*, **54**, 2859 (1932), and (c) Hellerman and Garner, *ibid.*, **57**, 139–143 (1935).

[2] Submission of this paper for publication has been delayed for some years. We appreciate the courtesy of F. G. Cottrell, former Chief of the Fixed Nitrogen Investigations Unit, Bureau of Chemistry and Soils, and of the late Julius Stieglitz, former Director of the George Herbert Jones Chemical Laboratory, The University of Chicago, for the use of certain facilities in connection with a portion of this work.