therefore, interpret the transformation as one involving the reaction of the methyl iodide with both the ethylate ions and the nonionized sodium ethylate.

2. The values $K_i = 0.127$ and $K_m = 0.0596$ agree well with those obtained for methyl iodide and potassium ethylate ($K_i = 0.126$ and $K_m = 0.0687$) by Dr. Julia Peachy Harrison, and for methyl iodide and lithium ethylate ($K_i = 0.1367$ and $K_m = 0.03871$) by Dr. J. H. Shrader. If the theory is correct the true values for K_i should be identical for all three ethylates and the same alkyl halide, and these studies and others, as a whole, confirm this conclusion.

3. The effect of an extra reaction, or "salt catalysis," on these reactions has been calculated.

4. A discussion of the reasons for working with various salts and alkyl halides shows that great care must be exercised in the final interpretation of these results. Chemical reactions are probably far more complex than we can realize with our present limited knowledge.

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ON THE REACTIONS OF BOTH THE IONS AND MOLECULES OF ACIDS, BASES AND SALTS.

A REINTERPRETATION OF THE REACTIONS OF SODIUM METHYLATE AND SODIUM ETHYLATE WITH 1,2-DINITROBENZENE, 1,2,4-DINITROCHLOROBENZENE AND 1,2,4-DINITROBROMOBENZENE.[1]

[TWENTY-SECOND[2] COMMUNICATION ON CATALYSIS.]

BY S. F. ACREE.

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The very fine work of Hecht,[3] Conrad and Brückner on the action of sodium ethylate on alkyl halides, and that of Bruyn, Steger,[4] and Lulofs[5] on the reactions of sodium methylate and sodium ethylate with the nitro and halogen substitution products of benzene were not interpreted by them by the use of the ionization theory. Conrad[6] and his co-workers spoke of these substances as nonelectrolytes, or "nichtleitende Körper." Bruyn and his co-workers, while measuring the conductivities of the sodium methylate and sodium ethylate, recognized that they were dealing with peculiar cases that could not be explained on the ionization hypothesis alone. In a footnote[7] Bruyn suggested that his reactions may

[1] We are indebted to the Carnegie Institution of Washington for aid in this work.

[2] See especially *Am. Chem. J.*, **48**, 352 (1912); **49**, 116, 127, 345, 369, 474 (1913).

[3] *Z. physik. Chem.*, **5**, 289 (1890). A similar reinterpretation of this excellent work will soon be published by Dr. W. A. Taylor.

[4] *Ibid.*, **49**, 329; **333**, 336 (1904); *Rec. trav. chim.*, **18**, 13, 41.

[5] *Z. physik. Chem.*, **49**, 341 (1904); *Rec. trav. chim.*, **20**, 292.

[6] *Z. physik. Chem.*, **5**, 289 (1890).

[7] *Rec. trav. chim.*, **18**, 40; see also *Z. physik. Chem.*, **49**, 332 (1904).

be different from those of Hecht, Conrad and Brückner and that, perhaps, "l'alcoholate s'unit d'abord au groupe AzO_2 par addition aet qu'a cette addition les molecules non dissociees prennent part exclusivement." They apparently overlooked the fact, however, that such a hypothesis must lead to a *decrease*[1] in the reaction velocity, K_N, as the concentration of the methylate or ethylate *decreases* and the percentage of non-*ionized electrolyte decreases*. As their reaction velocities never *decreased*, but remained constant or increased, their suggestion hardly meets the requirements of the mass law and the theory of ionization.

An inspection of the data in all these cases shows that *the reaction velocity is larger than that calculated on the hypothesis that the ethylate or methylate ions alone are active.* It was just such cases as these, and others, that lead the writer to see that this "deviation from the ionic reaction" could be due to the molecular sodium methylate or ethylate instead of to a so-called "salt catalysis," and to begin with Brunel in 1905, work on the theory that both the ions and nonionized forms of acids, bases and salts are chemically active.

The reactions discussed in this paper can be readily interpreted as transformations of both the anions and molecules of sodium ethylate and sodium methylate, as follows:

$$\overline{O}C_2H_5 + C_6H_4(NO_2)_2 \longrightarrow C_6H_4(NO_2)OC_2H_5 + \overline{N}O_2$$

$$NaOC_2H_5 + C_6H_4(NO_2)_2 \longrightarrow C_6H_4(NO_2)OC_2H_5 + NaNO_2$$

The equation $K_N = K_i\alpha + K_m(1 - \alpha)$, developed in earlier papers,[2] gives excellent constants for K_i and K_m in Table II of each section. The reaction velocities "K_N found" in Table I of each section are those recorded by Bruyn, Steger[3] and Lulofs. The ionization α, in Table I of each section, of the sodium ethylate is obtained from our own data,[4] while the ionization of the sodium methylate is obtained from Table V of S. Tijmstra Bz[5] by extrapolating to $M\infty = 85$ in absolute methyl alcohol and $\mu\infty = 80$ in 90.3% methyl alcohol. Since the values of K_m are very large in all cases, any small error in the ionizations resulting from this extrapolation will not invalidate the conclusion that the non-ionized methylate or ethylate is active. As the following table shows, the values of K_m are from 25% to 100% of those of K_i.

By substituting these values for K_i and K_m, and the proper ones for α in the equation $K_N = K_i\alpha + K_m(1 - \alpha)$, it is shown in Table I of each section in the experimental portion that the "K_N calculated" agrees

[1] *Am. Chem. J.*, **38**, 273 (1907); **39**, 226–231 (1908), and all the later papers.

[2] *Ibid.*, **39**, 226 (1908); **43**, 519 (1910) and later articles.

[3] *Z. physik. Chem.*, **49**, 331, 341, 342 (1904).

[4] *J. Phys. Chem.*, **19**, 381 (1915).

[5] *Ibid.*, **49**, 349 (1904).

	K_i.	K_m.	K_i/K_m.
Sodium ethylate and *o*-dinitrobenzene in absolute ethyl alcohol at 45°	0.229	0.230	1.0
Sodium methylate and *o*-dinitrobenzene in absolute methyl alcohol at 45°	0.1458	0.1278	1.2
Sodium methylate and 1,2,4-dinitrochlorobenzene in 90.3% methyl alcohol at 15°	1.376	0.759	1.8
Sodium ethylate and 1,2,4-dinitrobromobenzene in absolute methyl alcohol at 15°	1.299	0.724	1.8
Sodium ethylate and 1,2,4-dinitrobromobenzene in absolute ethyl alcohol at 15°	2.838	0.823	3.4
Sodium ethylate and 1,2,4-dinitrochlorobenzene in absolute alcohol at 15°	4.473	1.195	3.8

excellently with the K_N found experimentally by Bruyn, Steger and Lulofs, the "Error in percentage" in Table I of each section being generally small. The "percentage of reaction due to ions and to molecules" is given in Table III of each section.

Since the ethylate ion and the sodium ethylate molecules react with the same velocities with the *o*-dinitrobenzene, the change of the ethylate ions into the sodium ethylate molecules by the *addition of sodium nitrite and sodium acetate should have no effect on the reaction velocity:* this requirement of the theory is substantiated by the experiments,[1] and there is no noticeable "abnormal salt catalysis." Likewise the addition of sodium iodide to sodium ethylate and 1,2,4-dinitrobromobenzene *lowers* the reaction velocity, in conformity with the theory, because the *more active* ethylate ions are partially converted into the *less active* sodium ethylate molecules.[2]

The writer is greatly indebted to Dr. W. A. Taylor and Mr. E. C. White for making the calculations.

Experimental.

On the reactions of sodium ethylate and *o*-dinitrobenzene at 45°.

TABLE I.—THE IONIZATIONS, K_N CALCULATED AND FOUND, AND PERCENTAGE ERROR FOR SODIUM ETHYLATE AND *o*-DINITROBENZENE AT 45°.

V.	α.	$1-\alpha$.	K_N found.[3]	K_N calculated.	Error in per cent.
20	0.465	0.535	0.230	0.229	+0.4
40	0.563	0.437	0.229	0.229	0.0
60	0.631	0.369	0.229	0.229	0.0
80	0.670	0.330	0.230	0.229	+0.4
100	0.704	0.296	0.229	0.229	0.0

[1] *Z. physik. Chem.*, 49, 332 (1904).

[2] *Ibid.*, 49, 342 (1904).

[3] In this article we have used the values of K_N given, without attempting to verify them by recalculations or experiments.

TABLE II.—K_i AND K_m FOUND FOR SODIUM ETHYLATE AND *o*-DINITROBENZENE AT 45°.

	K_i.	K_m.
V = 20:V = 40	0.2245	0.2347
V = 20:V = 60	0.2270	0.2338
V = 20:V = 80	0.2300	0.2300
V = 20:V = 100	0.2277	0.2320
V = 40:V = 60	0.2290	0.2290
V = 40:V = 80	0.2290	0.2237
V = 40:V = 100	0.2321	0.2290
V = 60:V = 80	0.2385	0.2130
V = 60:V = 100	0.2290	0.2290
V = 80:V = 100	0.2203	0.2490
Average,	0.2287	0.2302

TABLE III.—PERCENTAGE OF REACTION DUE TO IONS AND TO MOLECULES.

V.	Percentage of reaction due to αK_i.	Percentage of reaction due to $(1-\alpha)K_m$.
20	46.4	53.6
40	56.2	43.8
60	63.0	37.0
80	66.9	33.1
100	70.3	29.7

On the reactions of sodium methylate and *o*-dinitrobenzene at 45°.

TABLE I.—THE IONIZATIONS, K_N CALCULATED AND FOUND, AND THE ERROR IN PER CENT. FOR SODIUM METHYLATE AND *o*-DINITROBENZENE AT 45°.

V.	α.	$1-\alpha$.	K_N found.	K_N calculated.	Error in per cent.
20	0.596	0.404	0.1385	0.1385	0.0
40	0.671	0.329	0.1400	0.1398	+0.1
80	0.734	0.266	0.1410	0.1410	0.0

TABLE II.—K_i AND K_m FOR SODIUM METHYLATE AND *o*-DINITROBENZENE AT 45°.

	K_i.	K_m.
V = 20:V = 40	0.1465	0.1265
V = 20:V = 80	0.1458	0.1277
V = 40:V = 80	0.1452	0.1293
Average,	0.1458	0.1278

TABLE III.—PERCENTAGE OF REACTION DUE TO IONS AND TO MOLECULES.

V.	Percentage of reaction due to αK_i.	Percentage of reaction due to $(1-\alpha)K_m$.
20	62.7	37.3
40	69.9	30.1
80	76.5	23.5

On the reactions of sodium methylate and 1,2,4-dinitrochlorobenzene in 90.3 per cent. methyl alcohol at 15°.

TABLE I.—THE IONIZATION, K_N CALCULATED AND FOUND, AND THE ERROR IN PER CENT. FOR SODIUM METHYLATE AND 1,2,4-DINITROCHLOROBENZENE AT 15°.

V.	α.	$1-\alpha$.	K_N found.	K_N calculated.	Error in per cent.
20	0.696	0.304	1.20	1.187	+1.09
33.33	0.742	0.258	1.21	1.216	—0.49
100	0.815	0.185	1.28	1.261	+1.50

TABLE II.—K_i AND K_m FOUND FOR SODIUM METHYLATE AND 1,2,4-DINITROCHLOROBENZENE AT 15°.

	K_i.	K_m.
V = 20 : V = 33.33	1.266	1.048
V = 20 : V = 100	1.404	0.732
V = 33.33 : V = 100	1.457	0.498
Average,	1.376	0.759

TABLE III.—PERCENTAGE OF REACTION DUE TO IONS AND TO MOLECULES.

V.	Percentage of reaction due to αK_i.	Percentage of reaction due to $(1-\alpha)K_m$.
20	80.6	19.4
33.33	83.9	16.1
100	88.8	11.2

On the reactions of sodium methylate and 1,2,4-dinitrochlorobenzene in absolute methyl alcohol at 15°.

TABLE I.—THE IONIZATION, K_N CALCULATED AND FOUND, AND ERROR IN PER CENT. FOR SODIUM METHYLATE AND 1,2,4-DINITROCHLOROBENZENE AT 15°.

V.	α.	$1-\alpha$.	K_N found.	K_N calculated.	Error in per cent.
20	0.661	0.339	1.10	1.104	—0.36
33.33	0.717	0.283	1.14	1.136	+0.35
100	0.805	0.195	1.18	1.186	—0.50

TABLE II.—K_i AND K_m FOUND FOR SODIUM METHYLATE AND 1,2,4-DINITROCHLOROBENZENE AT 15°.

	K_i.	K_m.
V = 20 : V = 33.33	1.342	0.627
V = 20 : V = 100	1.288	0.732
V = 33.33 : V = 100	1.268	0.814
Average,	1.299	0.724

TABLE III.—PERCENTAGE OF REACTION DUE TO IONS AND TO MOLECULES.

V.	Percentage of reaction due to αK_i.	Percentage of reaction due to $(1-\alpha)K_m$.
20	77.7	22.3
33.33	81.9	18.1
100	88.1	11.9

On the reactions of sodium ethylate and 1,2,4-dinitrobromobenzene in absolute alcohol at 15°.

TABLE I.—THE IONIZATION, K_N CALCULATED AND FOUND AND ERROR IN PER CENT. FOR SODIUM ETHYLATE AND 1,2,4-DINITROBROMOBENZENE AT 15°.

V.	α.	$1-\alpha$.	K_N found.	K_N calculated.	Error in per cent.
20	0.525	0.475	1.88	1.880	0.00
33.33	0.603	0.397	2.04	2.038	+0.09
100	0.749	0.251	2.33	2.332	—0.08

TABLE II.—K_i AND K_m FOUND FOR SODIUM ETHYLATE AND 1,2,4-DINITROBROMOBENZENE AT 15°.

	K_i.	K_m.
V = 20 : V = 33.33	2.854	0.803
V = 20 : V = 100	2.834	0.825
V = 33.33 : V = 100	2.828	0.842
Average,	2.838	0.823

TABLE III.—PERCENTAGE OF REACTION DUE TO IONS AND TO MOLECULES.

V.	Percentage of reaction due to αK_i.	Percentage of reaction due to $(1-\alpha)K_m$.
20	79.2	20.8
33.33	83.9	16.1
100	91.1	8.9

On the reactions of sodium ethylate and 1,2,4-dinitrochlorobenzene in absolute ethyl alcohol at 15°.

TABLE I.—THE IONIZATION, K_N CALCULATED AND FOUND, AND ERROR IN PER CENT. FOR SODIUM ETHYLATE AND 1,2,4-DINITROCHLOROBENZENE AT 15°.

V.	α.	$1-\alpha$.	K_N found.	K_N calculated.	Error in per cent.
20	0.5258	0.4742	2.94	2.92	+0.75
33.33	0.6037	0.3963	3.26	3.17	+2.74
100	0.7497	0.2503	3.56	3.65	—2.51

TABLE II.—K_i AND K_m FOUND FOR SODIUM ETHYLATE AND 1,2,4-DINITROCHLOROBENZENE AT 15°.

	K_i.	K_m.
V = 20 :V = 33.33	4.887	0.814
V = 20 :V = 100	4.253	1.484
V = 33.33:V = 100	4.279	2.019
Average,	4.473	1.195

TABLE III:—PERCENTAGE OF REACTION DUE TO IONS AND TO MOLECULES.

V.	Percentage of reaction due to αK_i.	Percentage of reaction due to $(1-\alpha)K_m$.
20	80.59	19.41
33.33	85.08	14.92
100	91.80	8.20

Conclusions.

The work of Bruyn, Steger and Lulofs on the reactions of sodium methylate and sodium ethylate on 1,2-dinitrobenzene, 1,2,4-dinitrochlorobenzene and 1,2,4-dinitrobromobenzene can be reinterpreted excellently as transformations of both the ethylate and methylate ions and the nonionized sodium ethylate and sodium methylate.

The value of K_m, the activity of the nonionized electrolyte per gram molecule per liter, is from 25% to 100% as large as the value of K_i, the activity of the methylate or ethylate ion per gram ion per liter.

These results harmonize excellently with (*a*) about 30 reactions which we have investigated experimentally, with (*b*) a large number of our reinterpretations of the work of others, and with (*c*) the results obtained recently by Arrhenius,[1] Goldschmidt,[2] Bredig,[3] Stieglitz,[4] Dawson,[5] Kilpi,[6] Holmberg,[7] Biddle[8] and Worley.[9]

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[1] Taylor and Arrhenius, *Memoirs of the Nobel Institute*, **2**, Nos. 34, 35, 37.
[2] *Z. Elektrochem.*, **15**, 6; *Z. physik. Chem.*, **70**, 627 (1910).
[3] *Z. Elektrochem.*, **18**, 535, 543; *Z. physik. Chem.*, **85**, 129, 170, 211 (1913).
[4] THIS JOURNAL, **34**, 1687, 1688, 1689, 1690, 1694 (1912); **35**, 1774 (1913).
[5] *J. Chem. Soc.*, **103**, 2135 (1913).
[6] *Z. physik. Chem.*, **86**, 427, 644, 740 (1914).
[7] *Ibid.*, **84**, 451, 468, 469 (1913).
[8] THIS JOURNAL, **36**, 99 (1914), and earlier papers.
[9] *Phil. Mag.*, **27**, 459.