

### Summary

1. The preparation of a number of dialkylaminomethyl ethers is described.

2. The mechanism of their hydrolysis to formaldehyde, alcohol and secondary amine has been studied and the conclusion reached that it involves the primary formation of N-dialkylmethyleneiminium ion, which subsequently adds hydroxide ion to yield the amine and formaldehyde.

3. N-Diethylmethyleneiminium chloride,  $(C_2H_5)_2N=CH_2Cl \cdot 6H_2O$  has been isolated. The platinum double salt,  $(iso-C_4H_9)_2N=CH_2)_2PtCl_6$ , has been prepared from the corresponding amino ether. It corresponds to the platinum double salt of Ehrenberg, prepared from tetraisobutylmethylene diamine.

4. The reaction between formaldehyde and diethylamine in dilute aqueous solution has been studied to confirm the mechanism of reaction of the amino ethers.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

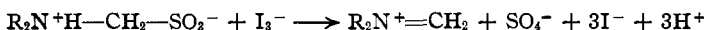
## THE RATE OF REACTION OF DISUBSTITUTED AMINOMETHYL SULFONIC ACIDS WITH IODINE

BY T. D. STEWART AND WILLIAM E. BRADLEY

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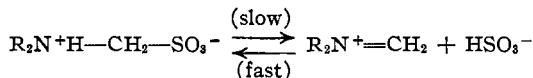
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The substituted aminomethyl sulfonic acids react with iodine in acid solution according to the equation



It has already been observed<sup>1</sup> that the reaction rate is independent of the iodine concentration, even for very low concentrations of iodine, and is first order with respect to the aminosulfonic acid. The rate is affected slightly by salts; the effect of increasing hydrogen-ion concentration up to about tenth normal is to decrease the rate; beyond that, up to one normal, there is but a small effect. At very low acidity the reaction is very fast and little or no iminium ion is formed.

The rate determining step appears to be the rate of ionization, represented as



The free sulfite ion at equilibrium is less than one per cent. In fairly concentrated solutions some indication of the dissociation is found. The reaction would appear to lend itself peculiarly well therefore to a study

<sup>1</sup> Stewart and Bradley, *THIS JOURNAL*, **54**, 4172 (1932), discuss this reaction and the evidence for the iminium ion.

of the effect of various substituents upon the reactivity of groups adjacent to the amino group.

**Discussion of Results.**—The experimental method is described in the next section. Under comparable conditions of ionic strength, acidity,

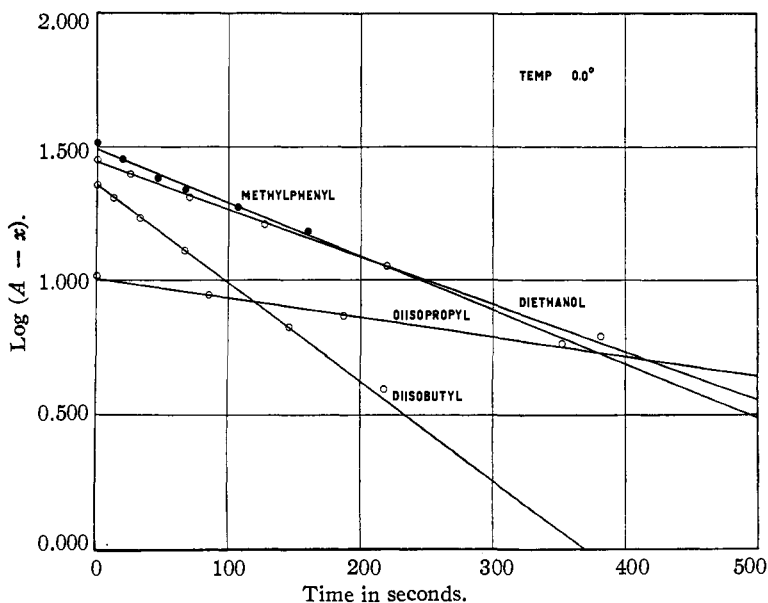


Fig. 1.—The reaction rate of disubstituted aminomethyl sulfonic acids (A) with iodine.  $(A - x)$  is expressed in cc. of iodine solution.

and temperature, a number of derivatives have been studied, and the results given in Figs. 1–4 and Table I. The names in Table I and on the plots refer to the two nitrogen substituents in the reactant. At 20° the

TABLE I  
THE REACTION RATES

Substituent groups	0.0°	Specific rate constants (sec. <sup>-1</sup> )		40.0°
		20.0°	30.0°	
Dimethyl		0.000272	0.00103	
Diethyl		.000750	.00271	
Di- <i>n</i> -propyl		.00265	.00923 (I <sub>2</sub> ) .00987 (Br <sub>2</sub> ) .00978 (H <sub>2</sub> O <sub>2</sub> )	
Diisopropyl	0.00172			
Di- <i>n</i> -butyl			.00666	
Diisobutyl	.00845			
Di- <i>n</i> -amyl			.00195	
Diallyl			.00893	
N-Piperidyl			.000554	0.00196
Diethanol	.00424	.0488		
Methylphenyl	.00474	.0484		

rate increases in the following order of the substituents: N-piperidyl (1), dimethyl (1.6), di-*n*-amyl (3.0), diethyl (4.4), di-*n*-butyl (10), diallyl (14), di-*n*-propyl (15), diisopropyl (120), phenylmethyl (280), diethanol (290), diisobutyl (570).

The rate is the same for the three oxidizing agents tried, namely, iodine, bromine, and hydrogen peroxide. This indicates an activated state common to each reaction, which is best represented by an ionization. Attempts to obtain a deviation from a first order law by using extremely

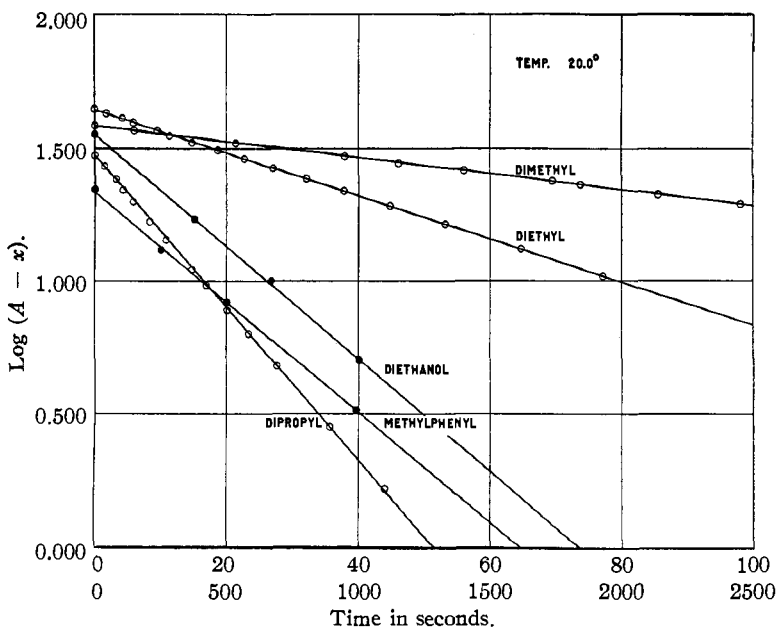


Fig. 2.—The reaction rate of disubstituted aminomethyl sulfonic acids (A) with iodine.  $(A - x)$  is expressed in cc. of iodine solution.

low iodine concentrations failed. If, however, the reaction rate were observed by adding measured quantities of iodine solution, noting the time necessary to use up that amount, and then waiting before the addition of more iodine, aberrations in the rate were observed. After such a pause in the addition of iodine, a small but detectable amount of iodine would be used up instantly. This confirms the assumption of an actual ionization as the rate determining step.<sup>2</sup>

The heats of activation have been calculated in the usual way and listed in Table II. It is seen that except for the last two, the increasing order of reactivities at 20° is the inverse of the increasing order of activation energies. The last two substances are anomalous in another respect.

<sup>2</sup> The alternative explanation would be a slow hydrolysis to an amino alcohol  $R_2NCH_2OH$ , followed by rapid iminium ion formation.

TABLE II

HEATS OF ACTIVATION			
Compound	$E$ , calcd.	Compound	$E$ , calcd.
N-Piperidyl	23,830	Di- <i>n</i> -propyl	22,030
Dimethyl	23,470	Diethanol	19,440
Diethyl	22,680	Phenylmethyl	18,500

If the logarithm of the specific reaction rate constant is plotted against the activation energy, a good straight line is obtained involving the first four compounds of Table II; the last two fall off the line. The accuracy of the measurements warrants considering this as suggestive of an unknown variable in the rate which involves part but not all of the compounds studied. In fact, referring to the order of reactivity given above,

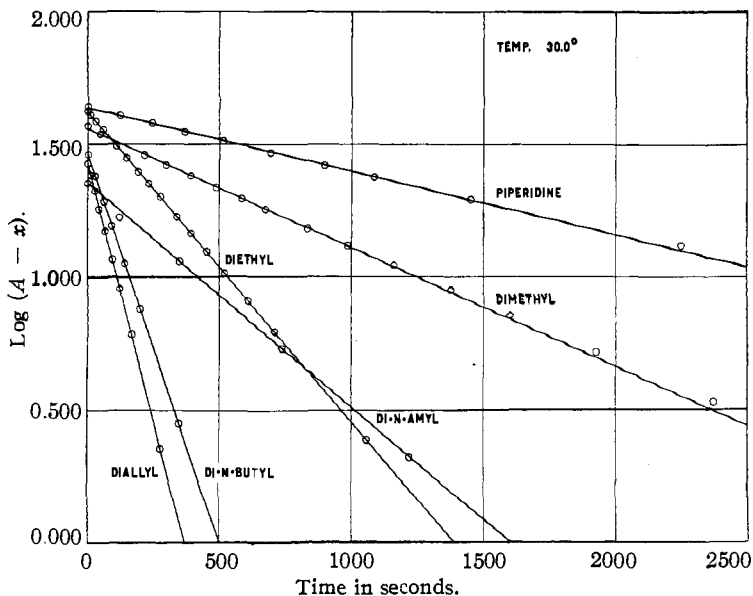


Fig. 3.—The reaction rate of disubstituted aminomethyl sulfonic acids (A) with iodine. ( $A - x$ ) is expressed in cc. of iodine solution.

the compounds seem to fall into two categories, those of high and those of low reactivity. Where the rates at  $20^\circ$  were not directly measured, or calculated from the measured activation energy, they were estimated by assuming the known activation energy of the substance having most closely the same reactivity.

The effect of the substituent groups in this reaction is probably exerted through the onium electron pair of the nitrogen atom and offers a valuable tool for the precise comparison of the effects of these groups upon chemical reactivity.

### Experimental Part

**Preparation of Materials.**—Preparation of the amino ethers has already been described.<sup>1</sup> The aminosulfonic acids were prepared from the corresponding amino ethers by the reactions

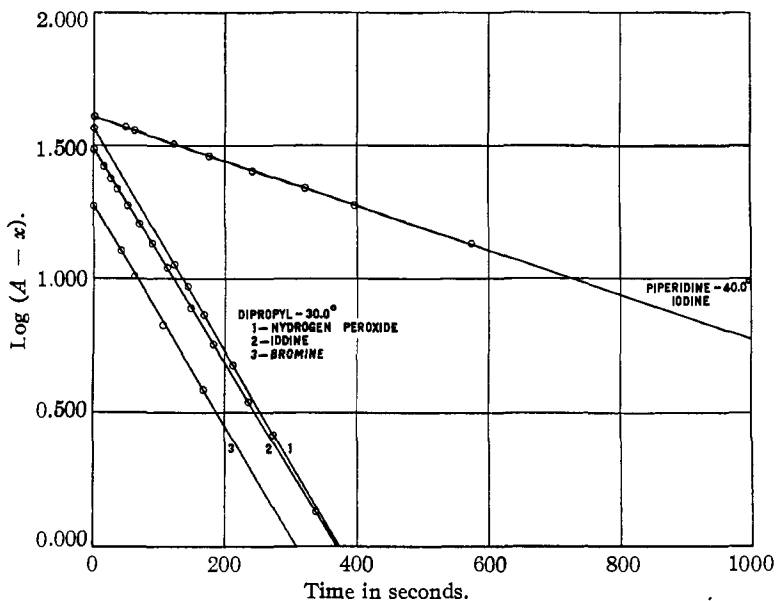
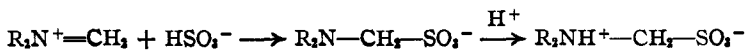
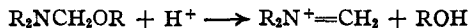


Fig. 4.—The reaction rate of disubstituted aminomethylsulfonic acids (A) with iodine, bromine and hydrogen peroxide.  $(A - x)$  is expressed in cc. of iodine solution.

TABLE III

#### DIMETHYLAMINOMETHYL SULFONIC ACID

Temperature of thermostat, °C.	20.00
Weight of dimethylaminomethyl <i>n</i> -butyl ether, g.	0.2854
Cc. of 0.1008 normal NaHSO <sub>3</sub> added	48.50
Cc. of 0.1008 normal I <sub>2</sub> <sup>-</sup> added into fading range	8.05
Cc. of 0.1008 normal I <sub>2</sub> <sup>-</sup> to permanent end-point	46.52

Elapsed time, sec.	Equivalents of reactant (in cc. of I <sub>2</sub> <sup>-</sup> )	Elapsed time, sec.	Equivalents of reactant (in cc. of I <sub>2</sub> <sup>-</sup> )
0	38.47	1835	22.96
149	36.65	2138	21.12
283	35.15	2450	19.44
534	32.85	2792	17.74
945	29.39	3150	16.12
1152	27.79	3640	14.12
1402	25.97	4127	12.40
1734	23.85	5018	9.72
			0.0

**Procedure.**—A weighed sample of the disubstituted aminomethyl ether was added dropwise to 15.00 cc. of 1.00 *N* hydrochloric acid which was agitated by means of a mechanical stirrer. An excess of approximately 0.1 *N* sodium bisulfite and 2.0 cc. of starch solution was added and the solution placed in a thermostat. A sufficient amount of a solution of approximately 0.1 *N* iodine was added to use up any ionized sulfite present. When the solution had come to the temperature of the thermostat, the rate was determined by adding successive small portions of iodine solution and noting the time required for the starch color to fade in each case. The total amount of iodine required to reach the permanent end-point was determined by following the reaction to completion. A typical example is given in Table III. This and similar cases are plotted in Figs. 1, 2, 3 and 4.

### Summary

The effect of various carbon groups upon the rates of ionization and heats of activation of disubstituted aminomethyl sulfonic acids has been studied.

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[CONTRIBUTION FROM THE PITTSBURGH EXPERIMENT STATION OF THE U. S. BUREAU OF MINES]

## THE THERMAL DECOMPOSITION OF METHANE BY A CARBON FILAMENT<sup>1</sup>

By H. H. STORCH<sup>2</sup>

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The writer has published elsewhere a brief, critical review<sup>3</sup> of the literature on the pyrolysis of methane. The thermal decomposition of methane in an isothermal, static system has recently been studied by Kassel<sup>4</sup> at temperatures low enough (700–850°) so that rate measurements on the early stages of the reaction were feasible. The reaction was found to be a homogeneous one of first order with a heat of activation of about 79,000 calories.

The experiments described in the present paper were all conducted in carbon filament lamps, the objectives being to isolate some of the early products of the pyrolysis of methane by immersing the walls of the bulb in liquid nitrogen or oxygen, and to avoid loss of hydrogen such as occurs in experiments with quartz bulbs. An additional objective was to study the reaction on a carbon surface rather than on quartz or metal surfaces coated with carbon.

<sup>1</sup> Published with the permission of the Director, U. S. Bureau of Mines. (Not subject to copyright.) Part of this work was presented at the meeting of the American Chemical Society at Buffalo, N. Y., in August, 1931.

<sup>2</sup> Principal physical chemist, U. S. Bureau of Mines, Pittsburgh Experiment Station, Pittsburgh, Pa.

<sup>3</sup> "Physical Chemical Properties of Methane," U. S. Bureau of Mines Information Circular 6549, January, 1932.

<sup>4</sup> L. S. Kassel. *THIS JOURNAL*, **54**, 3949 (1932).