differ greatly (somewhat smaller) from that obtained from conductance measurements. There is a close parallelism between the values obtained for the distance between charges from dielectric constant measurements and the strength of the electrolyte as indicated by conductance. Tetraisoamylammonium picrate is a much stronger electrolyte than triisoamylammonium picrate, although the latter is a slightly weaker electrolyte than silver perchlorate.[7] It would seem, therefore, that the phenomena occurring in solutions of electrolytes in a non-polar solvent are, in the main, controlled by coulomb forces. Under the action of these forces, the ions, existing predominantly free in extremely dilute solutions, associate to form, first, ion-pairs, and then more complex structures, neutral as well as charged, depending upon whether oppositely charged ions are present in equivalent amount. In the case of electrolytes having large symmetrical ions, the tendency to build up highly complex neutral structures is very pronounced.

Summary

Results of measurements are recorded for benzene solutions of tetraisoamylammonium picrate, triisoamylammonium picrate, tetraisoamylammonium bromide and silver perchlorate, chiefly between 10^{-4} and 10^{-3} N.

The limiting molecular polarization of these compounds is about ten times that of ordinary polar molecules, 2400 to 7800 cc.

The molecular polarization decreases rapidly with increasing concentration for salts with two electrically symmetrical ions and only slowly for salts with unsymmetrical ions.

The relation between the dielectric and other properties of these solutions is discussed.

Providence, R. I. Received July 20, 1934

[Contribution from the Chemical Laboratory of the Johns Hopkins University]

Ketene. III. Heat of Formation and Heat of Reaction with Alcohols

By F. O. Rice and Joseph Greenberg

Our first attempts to measure the heat of formation of ketene were by means of the reaction with water to form acetic acid. We found, however, that when ketene was passed into a calorimeter containing water, the initial rapid rise in temperature was followed by a slow rise, which continued for more than half an hour after the ketene had been passed in. This slow rise, which constituted from 5 to 10% of the total increase in temperature, is evidence of one or more side reactions. Ketene appears to react relatively slowly with cold water: apparently some of the ketene polymerizes to cyclobutadione-1,3 before it reacts with the water. We found acetone, which is one of the products of the hydrolysis of cyclobutadione-1,3, in the reaction mixture, and a quantitative estimation by Messinger's method[1] indicated that approximately 5% of the ketene had polymerized. Evidently the reaction between ketene and water is relatively slow and it is not surprising, therefore, that amino acids in aqueous solution can be acetylated with ketene.[2]

On the other hand, when ketene is passed into dilute aqueous sodium hydroxide in a calorimeter the final temperature is attained very rapidly and an estimate of the acetone present showed that only 1–2% of the ketene had polymerized. Since both the polymerization and hydrolysis of the polymer are exothermic reactions, the error from this source should be less than one per cent. We decided, therefore, to measure the heat of the reaction between dilute sodium hydroxide and ketene and use the value obtained for calculating the heat of formation of this compound.

Our calorimeter was of the Dewar type which has been described frequently.[3] A few modifications were necessary since we were studying the heat of the reaction between a gas and a liquid. At the beginning of an experiment the calorimeter contained a known amount of standard caustic soda at 0°. The Dewar flask containing this solution was surrounded by a coil of Pyrex glass and the whole was then packed in powdered ice. The ketene gas was first passed through this coil and then into the solution in the calorimeter. At the end of the experiment we titrated an aliquot portion of the solution, and

---

[1] Messinger, *Ber.*, **21**, 3366 (1888).

[2] Bergmann and Stern, *ibid.*, **63**, 437 (1930).

[3] Taylor, "Treatise on Physical Chemistry," D. Van Nostrand Co., New York, 1931, Chapter VI, p. 290.

from this we could calculate the amount of ketene added. Since we measured both the rise in temperature on addition of the ketene and the rise in temperature on addition of a known amount of electrical energy, we could calculate directly the heat of the reaction between the ketene gas and dilute aqueous sodium hydroxide; the results are given in Table I.

TABLE I

HEAT OF REACTION BETWEEN KETENE GAS AND DILUTE AQUEOUS SODIUM HYDROXIDE [APPROXIMATELY 0.05 *N*]

Columns 1–5 show, respectively, the moles of ketene added (*M*), the degrees rise in temperature on addition of the ketene (T_1), the current in amperes (i) which causes a rise in temperature of T_2° C. in t sec. *H* (column 6) is calculated from the formula $H = Ri^2tT_1 \times 0.2394/T_2 \times M$, R = resistance of heating coil = 6.83 ohms.

M	T_1	*i*	T_2	*t*	*H*
0.023860	1.890	1.220	2.061	498	46.60
.025255	2.055	1.230	2.080	501	47.40
.029775	2.360	1.280	2.413	540	47.50
				Mean	47.16

In order to calculate the heat of formation of ketene we used the following data[4]

$$\text{NaOH·aq} = \text{Na} + {}^1/_2\text{O}_2 + {}^1/_2\text{H}_2 + \text{aq.} - 112.5$$
$$\text{Na} + 2\text{C} + \text{O}_2 + 1{}^1/_2\text{H}_2 + \text{aq.} = \text{CH}_3\text{COONa·aq.} + 174.4$$
$$\text{CH}_3\text{COONa·aq.} = \text{CH}_2\text{CO(g)} + \text{NaOH·aq.} - 47.16$$

Addition of these gives the required equation for the heat of formation of ketene

$$2\text{C}_s + \text{H}_2 + {}^1/_2\text{O}_2 = \text{CH}_2\text{CO(g)} + 14.78$$

It is interesting to compare the heats of formation of ketene and of ethylene from the gaseous atoms. From the thermochemical equations[5]

$$
\begin{aligned}
&{}^1/_2\text{H}_2 = \text{H} - 51\\
&{}^1/_2\text{O}_2 = \text{O} - 59\\
&\text{C(graphite)} = \text{C (gas)} - 153\\
&2\text{C (graphite)} + 2\text{H}_2 = \text{C}_2\text{H}_4\text{(g)} - 6.5
\end{aligned}
$$

we obtain

$$
\begin{aligned}
&2\text{C(gas)} + 4\text{H(g)} = \text{C}_2\text{H}_4\text{(g)} + 503.5\\
&2\text{C(gas)} + 2\text{H(g)} + \text{O(g)} = \text{CH}_2{=}\text{CO(g)} + 481.8
\end{aligned}
$$

Heat of Reaction with Alcohols.—The heat of the reaction between ketene and methyl alcohol was measured in the same calorimeter as described above, with the exception that the top was sealed in order to avoid absorption of water by the absolute methyl alcohol. The amount of ketene that had been passed in was measured by hydrolyzing an aliquot portion of the contents of the calorimeter after the experiment with standard base and then titrating the excess base. The results are given in Table II.

TABLE II

HEAT OF REACTION BETWEEN KETENE GAS AND METHYL ALCOHOL

Columns 1–5 contain, respectively, the moles of ketene added (*M*), the degrees rise in temperature on addition of ketene (T_1), the current in amperes (i) which causes a rise in temperature of T_2° C. in t seconds. *H* is calculated from the formula $H = Ri^2t \times T_1 \times 0.2394/T_2 \times M$.

M	T_1	*i*	T_2	*t*	*H*
0.019778	2.306	1.290	2.222	250	36.52
.019554	2.249	1.280	2.249	279	36.42
.018137	2.007	1.340	2.310	259	36.40
				Mean	36.45

The best values for the heat of combustion of methyl alcohol and methyl acetate seem to be 174.0 Cal. and 381.2 Cal., respectively; assuming[6] the heat of solution of methyl acetate in methyl alcohol to be −1.0 cal.[7] we obtain for the heat of formation of ketene the value 14.73 Cal., which is in fair agreement with the value of 14.78 obtained from the heat of the reaction of ketene with aqueous sodium hydroxide.

The heats of reaction of ketene with several other alcohols were determined in an ice calorimeter; this apparatus has the great advantage of requiring only about 10 cc. of alcohol for each run. The calorimeter was exactly the same as the one used by Ramsay and Shields[8] and the principle and technique have been fully described elsewhere.[9] We calibrated the capillary to read directly in calories by passing a current of known amperage for a known length of time through a small resistance coil immersed in a small quantity of carbon tetrachloride in the calorimeter. In making a run, ketene was passed into the alcohol in the calorimeter sufficiently slowly that there was complete absorption and no ketene vapor collected in the space above the alcohol. After the final reading of the capillary was noted, the contents of the calorimeter were washed out and the amount of ketene added was determined by hydrolysis of the ester with an excess of standard alkali. The results for the different alcohols are shown in Table III.

It will be seen that the heat of reaction with ketene of all primary and secondary alcohols is 35 ± 2 Cal. The 4-carbon alcohols, in particular isobutyl and secondary butyl alcohol, show a slightly lower heat of reaction than this, but the

---

[4] Landolt–Börnstein, 1923, Berthelot's values.

[5] The first three values were taken from Kistiakowsky and Gershinowitz, *J. Chem. Physics*, **1**, 437 (1933), and the fourth from the "International Critical Tables."

[6] Rossini, *Bur. Standards J. Research*, **8**, 138 (1932); Roth and Bause, Landolt-Börnstein, 1931; Roth and Muller, *ibid.*, 1927.

[7] Estimated by comparison with the value for ethyl alcohol given in the "International Critical Tables."

[8] Ramsay and Shields, *Z. physik. Chem.*, **25**, 657 (1898).

[9] Taylor, "Treatise on Physical Chemistry," D. Van Nostrand Co., New York, 1931, Chapter on Thermochemistry.

TABLE III

HEATS OF REACTION OF KETENE WITH DIFFERENT ALCOHOLS

1.0 cm. of capillary, 2.641 Cal.; *M*, moles of ketene added; *D*, expansion of mercury in capillary.

Alcohol	*M*	*D*, cm.	*H*
Methyl	0.001240	17.57	36.8
Methyl	.001347	19.07	36.78
Methyl	.001213	17.39	37.23
		Mean	36.93
Ethyl	.001772	24.75	36.28
Ethyl	.001734	24.30	36.40
Ethyl	.001907	26.91	36.65
		Mean	36.44
n-Propyl	.001479	20.26	35.59
n-Propyl	.001629	21.93	34.98
n-Propyl	.00281	31.09	35.41
		Mean	35.32
Isopropyl	.001371	18.79	35.61
Isopropyl	.001929	26.87	36.19
Isopropyl	.001565	21.62	35.93
		Mean	35.91
n-Butyl	.001179	16.06	35.39
n-Butyl	.001863	25.03	34.90
n-Butyl	.001543	20.86	35.05
		Mean	35.11
s-Butyl	.002420	32.36	34.72
s-Butyl	.002546	33.89	34.57
s-Butyl	.002413	31.87	34.31
		Mean	34.53
Isobutyl	.001390	18.36	34.30
Isobutyl	.002248	29.87	34.51
Isobutyl	.002166	28.60	34.30
		Mean	34.37
t-Butyl	0.002960	27.05	23.74
t-Butyl	.002625	23.75	23.50
t-Butyl	.002542	22.75	23.25
		Mean	23.49

difference is not much greater than our experimental error. On the other hand, the heat of reaction of tertiary butyl alcohol is about 11 Cal. lower than that of the others. There was no perceptible odor of the polymer from the solution in the calorimeter after the experiment with tertiary butyl alcohol.

Summary

The heat of the reaction between ketene and dilute aqueous sodium hydroxide was measured; from this measurement we have calculated the heat of formation of ketene as: 2 C(graphite) + H_2(gas) + $^1/_2O_2$ (gas) = CH_2CO (gas) + 14.78 Cal.

The heat of reaction between ketene and different aliphatic alcohols was measured. The normal alcohols methyl, ethyl, propyl, butyl and isobutyl gave the values 36.93, 36.44, 35.32, 35.11 and 34.37 Cal. per mole, respectively. The secondary alcohols isopropyl and *s*-butyl gave the values 35.91 and 34.53 Cal. per mole, respectively. *t*-Butyl alcohol gave the much lower value of 23.49 Cal. per mole.

BALTIMORE, MD. RECEIVED JULY 21, 1934

[CONTRIBUTION FROM THE DEPARTMENT OF PHYSICAL CHEMISTRY, HARVARD MEDICAL SCHOOL]

Studies in the Physical Chemistry of Amino Acids, Peptides and Related Substances. II. The Solubility of α-Amino Acids in Water and in Alcohol–Water Mixtures

BY EDWIN J. COHN, THOMAS L. MCMEEKIN, JOHN T. EDSALL AND JOHN H. WEARE

I. Introduction.—Amino acids and proteins although not electrolytes, bear positive and negative charges, separated by a considerable distance, even when the molecule as a whole is electrically neutral. The powerful electric fields surrounding the charged groups give rise to important interactions with neighboring molecules and ions. Hence their behavior is in many respects strikingly similar to that of strong electrolytes. Besides these charged groups, however, the proteins and amino acids contain hydrocarbon chains and various ring structures found in other organic compounds. The volumes and the specific chemical characters of these groups also profoundly affect their behavior. In attempting to characterize amino acids and proteins in terms of their composition and structure, we can neglect neither the nature of the chemical groups that they contain, nor the electrical fields of force to which their neutral molecules give rise. In so far as the molecules are small in comparison with the charge that they bear, these substances will resemble electrolytes rather than non-electrolytes in their general behavior. In so far as the molecules are large and bear but a small number of electrical charges, their behavior will depend largely upon atomic configurations. At the one extreme, we have the smallest of the amino acids,