chemicals (bios) in the wort make this improvement. . . . .

"All our work on bios is based on the discovery that this substance is a mixture—not a mixture of different 'bioses' each adding to the yeast-crop—but a mixture of constituents none of which by itself has much effect. It is the addition of the last constituent (whichever it may be) to a culture-medium containing all the others that gives a good yeast-crop."

In addition to being a brilliant research man, Miller was a first-class teacher. The list of men who passed through his laboratory is quite impressive. Five well-known names are Robert Kennedy Duncan, Redman, Bray, Gortner and McBain, merely to mention a few. Miller is reported to have bought for his classes all the remaining copies of one edition of Gibbs. Nobody else has ever played on that scale.

Personally, Miller was clever, witty and kindly. Everybody recognized his charm. Physical chemistry in Canada owes more to Miller than to any other one man. This was recognized officially when he was elected an Honorary Member of the American Chemical Society in 1926.

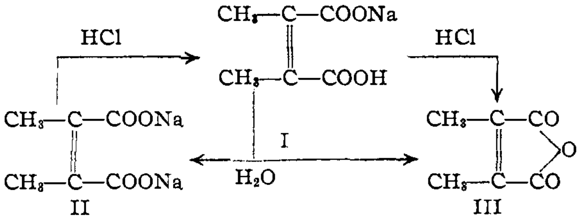
WILDER D. BANCROFT

[CONTRIBUTION FROM THE COBB CHEMICAL LABORATORY OF THE UNIVERSITY OF VIRGINIA]

Sodium Acid Dimethylmaleate

BY MONROE COUPER, CHARLES J. KIBLER AND ROBERT E. LUTZ

The possible existence of a monosodium acid salt of dimethylmaleic acid is a question of some interest because the free acid itself has not been isolated and when liberated from alkaline solution by acids, goes directly to the stable anhydride (III). An early attempt to prepare an acid salt failed.[1] The sodium acid salt (I) was discovered recently by accident. It is obtainable as a difficultly soluble crystalline precipitate when an aqueous solution of the disodium salt (II) is treated with one equivalent of hydrochloric acid. It decomposes when crystallization from water is attempted, giving disodium maleate and dimethylmaleic anhydride (III), but it can be crystallized successfully from dilute alcohol. Acidification immediately converts it into dimethylmaleic anhydride.



The instability of the acid salt probably accounts for the failure of previous investigators to obtain it.[1]

The precipitation of the acid salt proved to be of convenience in the large scale preparation of dimethylfumaric acid from dimethylmaleic anhydride. This reaction involves heating an aqueous solution of disodium maleate followed by separation of the resulting equilibrium mixture consisting of the disodium salts of dimethylmaleic and fumaric, and methylitaconic acids.[2] By precipitation of the acid salt (I) the bulk of the dimethylmaleic acid is separated from the mixture.

Experimental Part

Sodium Acid Dimethylmaleate (I).—Two grams of dimethylmaleic anhydride was added to a solution of 1.27 g. (two equivalents) of sodium hydroxide in 6.4 cc. of water. The mixture was brought exactly to neutrality toward phenolphthalein with hydrochloric acid. One equivalent (1.4 cc.) of concd. hydrochloric acid was then added and the acid salt crystallized rapidly in a yield of 1.6 g. (60%). The acid salt was re-crystallized as follows: it was dissolved in hot 60% ethanol; the solution was quickly cooled and filtered from the immediate precipitate which was contaminated with a little dimethylmaleic anhydride (this crop was discarded): 95% ethanol was then added, the monosodium acid salt crystallizing in pure condition as colorless square plates.

Anal. Calcd. for $C_6H_7O_4Na$: Na, 13.9; mol. wt., 166. Found: Na, 14.1; mol. wt. (by titration), 164.

Preparation of Dimethylfumaric Acid.—A solution of 800 g. of dimethylmaleic anhydride in 3 liters of water containing 508 g. (two equivalents) of sodium hydroxide, was heated in an autoclave at 188° for fifty-five hours. Two equivalents of concd. hydrochloric acid was added in six portions to the cold solution. After each addition of acid, the mixture was cooled thoroughly and the successive

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[1] Otto and Beckurts, *Ber.*, **18**, 833 (1885).

[2] Ott, *ibid.*, **61**, 2124 (1928); Lutz and Taylor, THIS JOURNAL, **55**, 1585 (1933).

crystalline precipitates removed by filtration. The first two crops consisted almost exclusively of the acid sodium salt of dimethylmaleic acid, and the third contained the remainder of this salt and some dimethylmaleic anhydride. These three fractions, combined and suspended in water, liberated dimethylmaleic anhydride upon addition of hydrochloric acid; yield 37%. The remaining three fractions from the original mixture consisted chiefly of dimethylfumaric acid; the first of these contained a small amount of dimethylmaleic anhydride which was removed by steam distillation. The yield of dimethylfumaric acid was 37%.

Repeated ether extraction of the filtrate from the above precipitations removed the methylitaconic acid which was obtained in a yield of 12%.

Summary

Sodium acid dimethylmaleate has been made by partial acidification of the disodium salt.

The precipitation of the monosodium salt has been used in the separation of products in the preparation of dimethylfumaric acid.

CHARLOTTESVILLE, VA. RECEIVED SEPTEMBER 27, 1940

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF NORTH CAROLINA]

The Interatomic Potential Curve and the Equation of State for Argon*

BY O. K. RICE

It has recently been stressed, that in order to obtain a good curve for the interatomic potential energy of a pair of atoms of a substance such as argon, it is necessary to take the properties of the solid into account. Buckingham[1] attempted to find a potential energy curve which would conform to a theoretical expression for large distances (obtained from refinement of London's theory of van der Waals forces), and would simultaneously correlate the heat of sublimation and lattice distance of the solid at 0°K. with the second virial coefficient for the gas. On the other hand, Herzfeld and Goeppert Mayer[2] and Kane[3] made calculations of the equation of state of the solid on the basis of preassumed potential curves. The potential curves used by them, however, were apparently not very satisfactory, since the calculated properties of the solid differed from the experimental in several important respects. A recently published calculation of a similar nature by Devonshire[4] did not take quantum effects into account.

As it appeared important, in connection with my recent studies on the fusion phenomena of argon, to have as accurate a potential energy curve as possible, it seemed that it would be worth while to construct a curve which would reproduce as well as possible the known properties of the solid from 0°K. to the melting point. At the same time it was desired that the curve pass into the theoretical expression of Buckingham for large distances, and also reproduce the second virial coefficient of the gas. This paper will present an attempt to construct such a curve, together with a discussion of the difficulties and uncertainties necessarily involved.

§1. Properties of the Solid in Terms of the Potential Energy Curve

We follow Buckingham in that we consider segments of the potential energy curve, assigning separate analytical expressions to the separate segments. We start by assuming Buckingham's form for the potential energy curve U at large interatomic distances, r, namely

$$U = -c_6 r^{-6} - c_8 r^{-8} \qquad (1)$$

with $c_6 = 60 \times 10^{-60}$ erg cm.^{6} and $c_8 = 180 \times 10^{-76}$ erg cm.^{8} for argon. These are slightly less than values, calculated by Buckingham,[5] which were stated to represent an upper limit. Reduced to more convenient units, we have

$$\begin{aligned} c_6 &= 8.64 \times 10^5 \text{ cal. mole}^{-1}\text{ Å.}^6 \\ c_8 &= 2.59 \times 10^6 \text{ cal. mole}^{-1}\text{ Å.}^8 \end{aligned} \qquad (2)$$

We assume that this potential can be used for all pairs of atoms which are not nearest neighbors.

For a short distance on either side of the minimum of the potential curve, we express U in the approximate form

$$U = U_0 + b_2 (r - r_0)^2 - b_3(r - r_0)^3 + b_4(r - r_0)^4 \qquad (3)$$

where U_0 and r_0 are the respective values of U and

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* Presented at the Fifth Annual Symposium of the Division of Physical and Inorganic Chemistry of the American Chemical Society, Columbia University, New York, December 30, 1940 to January 1, 1941.

(1) R. A. Buckingham, *Proc. Roy. Soc.* (London), **A168**, 264 (1938). See also J. Corner, *Trans. Faraday Soc.*, **35**, 711 (1939).

(2) K. F. Herzfeld and M. Goeppert Mayer, *Phys. Rev.*, **46**, 995 (1934).

(3) G. Kane, *J. Chem. Phys.*, **7**, 603 (1939).

(4) A. F. Devonshire, *Proc. Roy. Soc.* (London), **A174**, 102 (1940).

(5) R. A. Buckingham, *ibid.*, **A160**, 94 (1937).