concentration and acidification. The crude benzoylformic acid was a light yellow oil which weighed 12.6 g. It contained about 2 cc. of water which was removed as before. The crystalline benzoylformic acid obtained after purification weighed 7.5 g. (0.05 mole). This is a yield of 39%, based on the styrene content.

When drip oil fractions were taken which contained only 25% of styrene, oxidation to benzoylformic acid was not satisfactory.

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EVANSTON, ILL.   RECEIVED AUGUST 9, 1939

COMMUNICATIONS TO THE EDITOR

THE ENTROPY AND HEAT CAPACITY OF PROPYLENE

Sir:

Recently[1] Powell and Giauque have published measurements of the heat capacity of solid and liquid propylene which enabled them to determine the entropy change from 0°K. to the boiling point. By comparing this result with an entropy value calculated statistically on the basis of certain assumptions, they concluded that in solid propylene there is random end for end orientation of the molecules. This does not seem very reasonable to us a priori, inasmuch as one end is flat (CH_2), the other round (CH_3); one leg is considerably longer than the other and less polarizable; and finally the molecule has an appreciable dipole moment.[2] Furthermore their statistical calculations were based on a set of frequencies
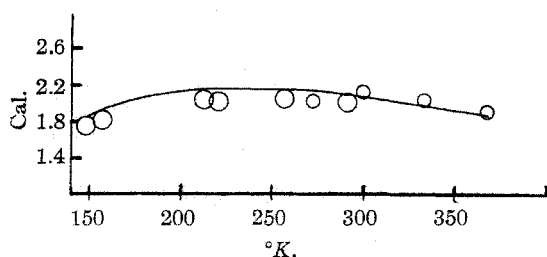

Fig. 1.—Calculated (solid line) and observed (circles) values of torsional heat capacity of propylene gas.

and a potential barrier hindering rotation of the methyl group (700 cal), published by one of us,[3] which are no longer acceptable. These frequencies were estimates obtained by comparison with other molecules, but on carrying the heat

(1) T. M. Powell and W. F. Giauque, THIS JOURNAL, 61, 2366 (1939).

(2) H. E. Watson, C. G. Rao and K. K. Ramaswamy, Proc. Roy. Soc. (London), 143, 558 (1934).

(3) G. B. Kistakowsky, J. R. Lacher and W. W. Ransom, THIS JOURNAL, 60, 900 (1938).

capacity measurements to higher temperatures it is found that the original set of frequencies would require a contribution from the internal torsional motion of the methyl group less than the classical value $1/2 R$, which is not plausible. Furthermore, an experimental study of the infrared and Raman spectra and a normal coördinate analysis has since been carried out, which, although not yet complete, shows that the estimated frequencies were not satisfactory. The revised frequencies lower somewhat the vibrational entropy at the boiling point, but the main effect is to raise considerably the potential barrier necessary to account for the heat capacity of the gas.

Before the publication of the entropy data we had reached the conclusion that a barrier of about 2000 cal. best fitted the heat capacity measurements when the revised frequencies were used. We have therefore calculated both the entropy at the boiling point and the gaseous heat capacity over a range of temperatures, using a barrier of 2119 cal. and the following frequencies: 432, 580, 921, 940, 1000, 1022, 1100, 1111, 1297, 1399, 1445, 1468(2), 1647, 3000(6) cm.$^{-1}$. Moreover, this calculation was carried out by a method which takes into account the complete dynamics of the molecule, including the coupling of the angular momentum of the top and of the whole molecule. This more complete calculation gave results differing from the values of Pitzer[4] by as much as 19% of the difference between free and hindered rotation. The heat capacities calculated are compared with those observed[5] in Fig. 1. The entropy of the ideal gas at the boiling point (225.35°K.) is calculated to be 59.87 cal., compared with the experimental value of 59.93 cal.

(4) K. S. Pitzer, J. Chem. Phys., 5, 469 (1937).
(5) From ref. 3 and unpublished work.

obtained by assuming *no random orientation* in the solid. The agreement is well within the possible theoretical uncertainties and therefore we do not need, on the basis of the available evidence, to make the assumption that the third law breaks down for this substance.

Further details of the measurements on the heat capacities, on the study of the vibration frequencies, and on the method of calculating thermodynamic properties for molecules containing hindered rotators will be published separately. It should be noted that the vibration frequencies used herein are still provisional so that the value 2120 cal. for the potential barrier is not final; it does, however, correlate all the data now available. It further indicates that 59.93 E. U. is the proper value of the entropy at the boiling point.

HARVARD CHEMICAL LABORATORY   B. L. CRAWFORD, JR.[6]
CAMBRIDGE, MASS.   G. B. KISTIAKOWSKY
                                        W. W. RICE
                                        A. J. WELLS
                               E. B. WILSON, JR.
RECEIVED SEPTEMBER 22, 1939

A PHOTOCHEMICAL PRODUCTION OF REDUCING SUGARS FROM GLYCOSIDES BY ULTRAVIOLET LIGHT

Sir:

Ultraviolet light absorbed by fructosides and glucosides liberates reducing sugars.

A special arrangement of apparatus soon to be published in *Science* made it possible to illuminate aqueous solutions of these glycosides in thermostated quartz tubes where 11 or 12 cc. absorbed about 10^{19} photons of λ 254 mμ per minute. The light flux was measured with the uranyl oxalate actinometer. Portions of the solutions were kept in the dark at the same temperature as the illuminated portions and analyses were made on all portions at the same time and under the same conditions. The ml. of 0.002 M sodium thiosulfate entered as hypo in Table I represent the difference between Shaffer–Hartmann–Somogyi (S.–H.–S.) estimations on the dark and illuminated solutions, although the dark reaction was usually negligible. One ml. of hypo was equivalent to 5.6×10^{-5} g. of glucose or 6.1×10^{-5} g. of fructose acid which was reproduced to 0.1 ml. Professor C. B. Purves kindly supplied the glycosides as pure crystals.

Solutions were water white after these photolyses, but the solutions titrated with hypo were sometimes a light amber at the end-point as, for example, in Expts. 3 and 5. Also, strongly photolyzed solutions turned amber after a day or more in the dark at room temperature. The differences in the photochemical efficiencies of the α and β isomers are significant.

The change in the optical activity accompanying the formation of the reducing sugar was measured for solutions of β-benzylfructopyranoside. Rotations of the D lines of sodium were read to 0.02° in a four-decimeter tube at 21.5°.

In a typical experiment, a molar acetate solution at pH 3.5 contained 1.8016 g. of β-benzylfructopyranoside in 100 cc. The initial rotation of the solution was $-9.45°$ and the change expected for complete hydrolysis was 5.1° to give a rotation of $-4.35°$. Three samples illuminated at 10° with light of λ 254 mμ gave observed rotations of -9.00, -8.77 and $-8.56°$, corresponding to 9, 14 and 18% hydrolysis; and the estimations of reducing sugar gave 9, 13.5 and 18% respectively. The corresponding percentages agree within the limits of error. The calculations based on the S.–H.–S. estimations assumed the

TABLE I

Typical data on glycosides at 0.02 M in water; temperature, 23°; volume illuminated, 11 cc.; pH of solutions not photolyzed, 6.2; light flux per minute, 8.6×10^{18} photons of λ 254 mμ.

Expt.	Glucopyranosides	pH after photolysis	Minutes photolyzed	Hypo, ml.
1	α-Phenyl	3.5	47	6 $\times$ 11/5 = 13.2
2	β-Phenyl	3.5	47	8.8 $\times$ 11/5 = 19.4
3	α-Benzyl	4.2	64	27.6 $\times$ 11/5 = 60.8
4	α-Benzyl	...	30	16.2 $\times$ 11/5 = 35.6
5	β-Benzyl	3.7	64	11.2 $\times$ 11/2 = 61.5
6	β-Benzyl	...	29	18.2 $\times$ 11/5 = 40.0
7	β-(β-Phenylethyl)	4.4	82	7.05 $\times$ 11/2 = 38.8
8	β-(β-Phenylethyl)	...	32	11.8 $\times$ 11/5 = 26.0
	Fructopyranoside			
9	β-Benzyl	4.5	40	6.4 $\times$ 11/2 = 35.0