[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

The Base Strengths and Absorption Spectra of *p*-Methylacetophenone and *p*-Bromoacetophenone

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We have determined the base strengths of *p*-methylacetophenone and *p*-bromoacetophenone by a method which has been described previously[1] and which involves the measurement of the ultraviolet absorption spectra of solutions of these substances in various mixtures of sulfuric acid and water.

The *p*-methylacetophenone was purified by six fractional distillations under reduced pressure, and boiled at 75.5–76° at 2.5 mm. The *p*-bromoacetophenone was recrystallized from alcohol–water and melted at 51–51.5°. The absorption spectra were determined exactly as in the previous work,[1] and the results are collected in Tables I and II. The effect of changing sulfuric acid concentration is much the same for all three substances except that the region of ionization appears at smaller acid concentrations with the methyl derivative and at larger concentrations with the bromo derivative than with the parent substance.

The calculations of base strength were made by the "isobestic point" method. For the methylacetophenone the reference solutions were 52.0 and 83.5% sulfuric acid and the isobestic point was taken at a wave length of 2800 Å. and an absorption coefficient of 9600. For the bromoacetophenone the corresponding figures were 60.1, 90.9%, 2920 Å., and 11,300.

TABLE I

EXTINCTION COEFFICIENTS AND BASE STRENGTH OF *p*-METHYLACETOPHENONE

Wave length, Å.	%, H_2SO_4								
	0	52.0	65.2	67.9	70.5	73.7	80.4	83.5	96.0
3700						110	200	230	420
3600				140	200	330	580	670	1100
3500			230	360	570	870	1480	1680	2500
3400			600	920	1400	2200	3500	3700	5500
3300		120	1400	2400	3400	4800	7500	8000	11000
3200	90	340	3250	5100	7050	10100	13800	15200	18500
3100	190	900	5900	8800	11700	15300	19500	20700	23800
3000	490	2100	8300	11000	13700	16300	18200	18600	17500
2900	1350	4150	9200	10800	11900	13300	12500	12000	9400
2800	3200	7000	9800	10300	9700	8900	6700	5100	4000
2700	7500	11300	10000	9100	7400	5700	2800	2100	1200
2600	12900	13300	9000	7600	5600	3500	1200	810	350
2500	12700	10000	(5600)	4800	3000	1800	420	250	110
2400	7500	4900	(2400)	(1800)	(1300)	700	250	200	190
2300	2600	1600	(970)	(890)	(800)				
H°		−3.45	−4.90	−5.24	−5.60	−6.00	−6.88	−7.40	−8.88
			pK'						
pK'			−5.35 ±0.07	−5.34 ±0.06	−5.37 ±0.07				

Average value of *pK'*, −5.35.

It is worthy of note that the spectra of both of these *p*-substituted acetophenones differ from that of acetophenone in that they lack the weaker band which produces a shelf on the long wave length side of the principal absorption band of the latter substance. The single band observed in the substituted derivatives is, however, in the same region and of about the same strength as the principal band of acetophenone. The effect

From previous experience[2] the effects of nuclear substituents upon the free energy of the basic ionization of acetophenone may be expected to be linearly related to their effects upon the free energy of reaction or of activation of other side chain reactions of benzene derivatives. Actually the deviation from linearity is considerable, which is not surprising in view of the small number of points and the relatively low precision of the

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[1] Flexser, Hammett and Dingwall, THIS JOURNAL, **57**, 2103 (1935).

[2] (a) Hammett, *ibid.*, **59**, 96 (1937); (b) Hammett, *Trans. Faraday Soc.*, **34**, 156 (1938).

TABLE II

EXTINCTION COEFFICIENTS AND BASE STRENGTH OF *p*-BROMOACETOPHENONE

Wave length, Å.	%, H_2SO_4							
	0	60.1	73.7	76.2	78.4	80.4	90.9	96.0
3700							100	130
3600			70	130	170	260	740	1250
3500			420	730	1200	1850	5200	6500
3400		80	1850	3300	4800	6600	14500	18000
3300	60	180	4600	7300	10000	12500	22000	24500
3200	100	490	7000	10600	13900	17000	23100	13800
3100	160	1150	9200	12200	14700	17000	19000	17900
3000	350	2700	10600	11700	12800	13800	12100	10000
2900	1600	5700	11300	11200	10700	10000	6100	4700
2800	4300	10000	11700	10200	8500	7000	2800	2000
2700	11000	15000	11300	8500	6400	4800	1200	860
2600	16700	14900	8300	6100	4400	2900	600	440
2500	13500	8800	4600	3200	2100	1450	360	305
2400	6600	4000	1700	1300	1050	840	700	980
$H°$		−4.33	−6.00	−6.30	−6.58	−6.88	−8.27	−8.88
			pK'					
pK'			−6.40 ±0.17	−6.38 ±0.08	−6.38 ±0.13	−6.45 ±0.10		

Average value of *pK'*, −6.40.

method of measurement. Nevertheless, it may be said with certainty that this is a reaction in which substituents have large effects, the best value of the reaction constant ρ being −2.56 (in terms of the basic ionization) with a "probable error" of 0.12. That is to say, the effect of a substituent upon the quantity *pK'* of acetophenone is approximately 2.56 times as great as its effect upon the *pK* of benzoic acid. This is in interesting contrast with the effects of substituents upon rate of the acid catalyzed bromination of acetophenone,[3] which undoubtedly proceeds by way of the same basic ionization, and for which the value of ρ is only −0.55.[2a]

Summary

We have measured the ultraviolet absorption of solutions of *p*-methylacetophenone and of *p*-bromoacetophenone in various mixtures of sulfuric acid and water, and have derived therefrom values of the base strengths of these ketones. The effect of substituents upon the free energy of the basic ionization of acetophenone is of the order of −2.56 times the effect upon the acid ionization of benzoic acid.

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[3] Nathan and Watson, *J. Chem. Soc.*, 217 (1933); Evans, Morgan and Watson, *ibid.*, 1167 (1935).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY]

The Synthesis of Crystalline 6-[*β*-*d*-Glucosido]-*α*-*d*-mannose, the Epimer of Gentiobiose, and its Octaacetate[1]

BY HYP J. DAUBEN, JR., AND WM. LLOYD EVANS

Although several epimeric pairs of disaccharides have been synthesized and their properties carefully studied, they have been exclusively of the 4-linked type. No 6-linked epimeric pair has been reported. Foreseeing the possible problems which would arise from such a synthesis, gentiobiose was epimerized by the glycal-oxidation method of Bergmann and Schotte[2] to give 6-glucosidomannose, *i. e.*, epigentiobiose. This afforded the first application of this method of synthesis to 6-linked disaccharides and at the same time offered an opportunity to observe whether the *cis* epimer (*cis* C_2-C_3 configuration) was formed in preponderance by this type of saccharide.[3]

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[1] This paper is based upon a thesis submitted by Hyp J. Dauben, Jr., to the Graduate School of The Ohio State University in partial fulfilment of the requirements for the degree of Master of Science.

[2] Bergmann and Schotte, *Ber.*, **54**, 440 (1921).

[3] Levene and Tipson, *J. Biol. Chem.*, **93**, 631 (1931).