β-isomers give identically quantitative yields of the same compound. In the 4-methoxy compounds, the yields are neither quantitative nor equal, but apparently, judging from the spectra obtained, the other products are not hydroxymethoxyazobenzenes. Probably side reactions occurring at different rates complicate the reaction. The findings thus seem to confirm the Russian workers proposed mechanism involving a three-membered ring intermediate.[7]

The most unexpected finding is that, whereas the oxygen atom migrates to the free *p*-position in both the 4-bromo- and 4-methoxy compounds, it migrates to an *o*-position (in the unsubstituted ring) in the 4-methyl compound. This is even more surprising since the electronic effect of the methyl group is generally considered intermediate between the bromo and methoxy groups. No explanation for this surprising finding can be offered at this time. It is conceivable that minor differences in reaction conditions give rise to the observed differences in behavior. This possibility, however, is extremely unlikely because the reactions are so clean, giving no indication that mixtures are obtained. The question is being investigated further.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CINCINNATI, CINCINNATI, OHIO]

The Basicities of Substituted Azoxybenzenes[1]

BY CHI-SUN HAHN[2] AND H. H. JAFFÉ

RECEIVED APRIL 27, 1961

The basicities of sixteen 4-, 4'- and 4,4'-substituted azoxybenzenes were determined. The effect of substituents on the basicities of these compounds and the structure of the conjugate acid of azoxybenzenes are discussed.

Although a tremendous amount of work has been concerned with the structure and stereochemistry of the azoxy group,[3] particularly in azoxybenzene and its derivatives, little is known about the physico-chemical behavior of this group. In connection with studies in this Laboratory of the base strengths of azobenzene derivatives[4] and of other weak nitrogen bases and their N-oxides,[5] we have now undertaken an investigation of the base strengths of azoxybenzene and substituted azoxybenzenes, about which no previous work has been reported. The pK_a's of the conjugate acids of the parent compound, four symmetrically disubstituted, nine monosubstituted and two unsymmetrically disubstituted derivatives were determined by a standard spectrophotometric method[6] in 20% ethanolic solution of sulfuric acid.[4]

Experimental

Compounds.—All the azoxybenzenes under investigation are 4-, 4'-mono- and 4,4'-disubstituted compounds, which were prepared by oxidation of the appropriate azobenzene derivatives.[7] The azobenzenes, in turn, were prepared by condensation of anilines and nitrosobenzenes.[8] The anilines were commercially available; the nitroso compounds were prepared by reduction and oxidation from nitro compounds.[9] Oxidation of the azo compounds, in general, produces mixtures of α- and β-azoxybenzenes, which were separated by chromatography on columns of alumina. The compounds were repeatedly recrystallized, usually from aqueous alcohol, until melting points were unchanged and agreed with literature values. The compounds and their melting points are listed in Table I.

Spectrophotometric and Acidity Measurements.—The methods used were substantially the same as those previously described.[4] The spectra of the various compounds, in neutral and acid solution, were recorded using a Cary model 11 spectrophotometer. Titration curves at selected wave lengths (ϵ *vs.* H_0) were determined using a Beckman model DU quartz spectrophotometer. Although at the wave lengths used in the work on azo compounds,[4] water was found to be adequate as material in reference cells, at the wave lengths used in the present work, particularly below 250 mμ, preliminary work showed that it was essential to have solutions having the same water-sulfuric acid-ethanol ratio in the reference cell as in the sample compartment. Consequently, reference solutions were prepared just like sample solutions, omitting the azoxy compound.

Preparation of Solutions.—Solutions (5×10^{-5} *M*) of the azoxy compounds in a solvent consisting of 20% ethanol and 80% sulfuric acid-water mixture of various composition were required for the determination of the titration curves. In the preparation of such solutions, considerable heat is obviously evolved. In our previous work with azo compounds we had found that reproducible results could be obtained by mixing precooled 10^{-4} *M* stock solutions of the substrate with precooled and premixed water-sulfuric acid mixtures in an ice-bath, provided the process was performed slowly. Similar mixing of azoxybenzene stock solutions with sulfuric acid-water mixtures invariably led to solutions containing various amounts of hydroxyazo compounds, formed by the Wallach rearrangement,[10] when the sulfuric acid in the aqueous component exceeded about 50%. Thus occurrence of the Wallach rearrangement could not be prevented by cooling to lower temperatures or by slowing down additions, and is believed to be due to local heating at the point where a drop of one solution first comes in contact with the other. The technique of using a single stock solution was considered highly desirable because it ensures constant

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[1] This work was supported jointly by a Grant in Aid from the American Cancer Society, and by the Office of Ordnance Research, U. S. Army.

[2] Abstracted from the University of Cincinnati Ph.D. thesis of C.S.H.

[3] A. Angeli and L. Alessandri, *Atti. Accad. Lincei*, **20I**, 896 (1911); **20II**, 170 (1911); A. Angeli and Bruno Valori, *ibid.*, **21I**, 155, 729, 794 (1912); A. Angeli and D. Bigiavi, *ibid.*, [6] **5**, 819 (1927); N. Zinin, *Ann.*, **114**, 222 (1860); A. Werner and E. Stiasny, *Ber.*, **32**, 3262 (1899).

[4] H. H. Jaffé and R. W. Gardner, *J. Am. Chem. Soc.*, **80**, 319 (1958); G. S.-J. Yeh and H. H. Jaffé, *ibid.*, **81**, 3274 (1959); J. H. Collins, unpublished results.

[5] H. H. Jaffé, *J. Am. Chem. Soc.*, **76**, 3527 (1954); H. H. Jaffé, *J. Org. Chem.*, **23**, 1790 (1958); E. Barber, M.S. thesis, University of Cincinnati, 1961.

[6] L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, p. 267.

[7] A. Angeli, *Atti. Accad. Lincei*, **19I**, 793 (1910); A. Angeli and Bruno Valori, *ibid.*, **22I**, 132 (1913).

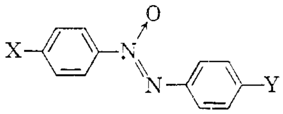
[8] C. Mills, *J. Chem. Soc.*, **67**, 929 (1895).

[9] G. H. Coleman, C. M. McCoskey and F. A. Stuart, in "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1955, p. 668.

[10] O. Wallach, *Ber.*, **13**, 525 (1880).

TABLE I

THE MELTING POINTS OF SUBSTITUTED AZOXYBENZENES[a]



X	Y[g]	M.p., °C. (obsd.)	M.p., °C. (lit.)	Ref.
H	H	36	36	k
CH_3	CH_3	71-72	70.5-71.5	b
Cl	Cl	154-155	155	c
Br	Br	175-176	175	d
OCH_3	OCH_3[h]	117-118	117.4-118.5	e
H	CH_3	46-48	46	f
CH_3	H	65	65	f
Cl	H	62-63	62	j
H	Br	73-73.5	73	3
Br	H	92-92.5	92	3
H	OCH_3[w]	66.5-67.5	x	
OCH_2	H[w]	42-43	y	
H	OC_2H_5[i]	72	72	3
H	NO_2	152-153	153	3
CH_3	Br	114	112	f
Br	CH_3	122-123	z	

[a] All compounds are *trans* isomers. [b] E. Bamberger, *Ber.*, **59**, 427 (1926). [c] K. Heumann, *ibid.*, **5**, 911 (1872). [d] A. Werige, *Ann.*, **165**, 198 (1873). [e] A. Prins, *Z. physik. Chem.*, **67**, 720 (1909). [f] D. Bigiavi and V. Sabatelli, *Gazz. chim. ital.*, **57**, 557 (1927). [g] All compounds were recrystallized from aqueous EtOH except where otherwise noted. [h] Recrystallized from ligroin–EtOH. [i] Recrystallized from ligroin. [j] V. O. Lukashevich, *Compt. rend. acad. sci. U.R.S.S.*, **21**, 376 (1938); *C. A.*, **33**, 3769 (1939). [k] A. Angeli, *Atti. Accad. Lincei*, **19I**, 793 (1910); **22I**, 132 (1913). [w] The stereochemistry of these two compounds was assigned by comparison of their ultraviolet spectra with those of L. Szegö, *Ber.*, **61**, 2090 (1928), who had not reported melting points. [x] *Anal.* Calcd.: C, 6840; H, 5:30; N, 12.28. Found: C, 68.0; H, 5.3; N, 12.6. [y] *Anal.* Calcd.: C, 68.40; H, 5:30; N, 12.28. Found: C, 68.4; H, 5.2; N, 12.4. [z] *Anal.* Calcd.: C, 53.62; H, 3.81; N, 8.63. Found: C, 52.7; H, 3.7; N, 9.1. The stereochemistry of this compound follows from the fact that the ultraviolet spectrum characterizes it as a *trans*-azoxy compound, and that the other isomer ($X = CH_3$, $Y = Br$) is known.

substrate concentration in all solutions, and hence was felt essential. A successive mixing scheme was finally evolved, in which precooled portions of successively more concentrated sulfuric acid–water mixtures were successively added to 10 ml. of a precooled 10^{-4} *M* stock solution of the azoxy compound in 95% ethanol in a 50-ml. volumetric flask. Four steps were generally used, and all solutions were kept cold in a Dry Ice–acetone-bath. Only before the last addition, bringing the solution to final volume, was the solution brought to 25° in a constant temperature bath. Table II shows the steps used in this dilution process; the first column gives the nominal H_2SO_4 concentration, *i.e.*, the approximate H_2SO_4 concentration in the aqueous portion of the solvent. Under each of the four steps are then listed the volume and the composition of the aqueous sulfuric acid used in vol. %. The solutions were brought to the mark with sulfuric acid of the nominal concentration. This stepwise procedure was successful in preventing the Wallach rearrangement. The final acid concentrations obtained were determined by density measurements.

Results and Discussion

The pK_a's of the conjugate acids of all the azoxybenzenes investigated are listed in Table III. Inspection of the table immediately shows that electron-releasing substituents generally increase, electron-withdrawing substituents decrease the base strength of azoxybenzenes, as expected.

TABLE II

STEPWISE PROCEDURE OF THE PREPARATION OF SOLUTION

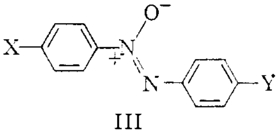
Nominal final concn. %	1st step ml.	%	2nd step ml.	%	3rd step ml.	%	4th step ml.	%
40	5	30	5	40	20	40	9	45
60	5	30	5	50	9	60	18	70
70	5	30	5	70	9	70	18	80
80	5	30	5	70	9	80	18	93
90	5	40	5	80	9	100	18	100

Quantitative treatment of these substituent effects can be achieved through the "Hammett equation" in a variety of ways. The most obvious procedure is to apply the Hammett equation separately to the series of 4-substituted,[12] and to the series of 4′-substituted compounds. These treatments would use, repectively, the equations

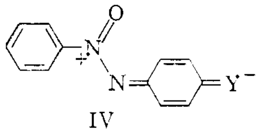
$$\log (K_{xo}/K_{oo}) = \sigma_x \rho_x \qquad (1)$$

$$\log (K_{oy}/K_{oo}) = \sigma_y \rho_y \qquad (2)$$

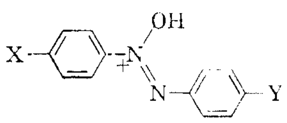
where K_{oo}, K_{xo} and K_{oy} represent, respectively, the equilibrium constants for azoxybenzene, its 4-X and 4′-Y derivatives. The question then arises which type of σ-value, the normal σ, σ^+ or σ^-, would be appropriate. Examination of resonance structures of azoxybenzene and its conjugate acid immediately shows that no low energy structures can be written in which a *positive* charge can be mesomerically shifted into either the 4- or 4′-substituent, and no *negative* charge can be shifted into the 4-substituent. Hence the normal σ-value must be appropriate for X. On the other hand, the resonance III $\leftrightarrow$ IV is likely to be important in the free base, and the resonance V $\leftrightarrow$ VI, because of the increased number of charges and the proximity of two *positive* charges, should be much less important in the conjugate acid. But this change in relative importance of structures like IV and VI between free base and conjugate acid is just the condition for applicability of σ^- constants, and hence these constants seem appropriate for use for Y. Unfortunately only one compound, the 4′-nitro derivative, is capable of



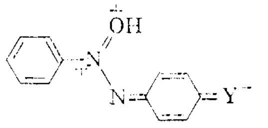
III



IV



V



VI

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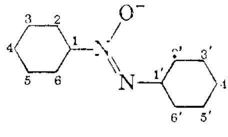
(11) Reference 6, Chapter 7; H. H. Jaffé, *Chem. Revs.*, **53**, 191 (1953).

(12) For purposes of this discussion, we number azoxybenzene as



and call a general substituent in the 4-position X, in the 4′-position Y.

TABLE III

THE *pK*'S OF AZOXYBENZENES

		X = MeO	X = Me	X = H	X = Cl	X = Br
		−p*K*	−p*K*	−p*K*	−p*K*	−p*K*
Y	σ_y^{-}[11]	σ_x −0.268	−0.170	0	0.227	0.232
MeO	−0.268	5.23 ± 0.03		6.10 ± 0.04		
EtO	− .250			6.04 ± .03		
Me	− .170		5.47 ± 0.05	6.04 ± .03		6.90 ± .03
H	.000	6.15 ± .04	6.16 ± .04	6.45 ± .05	6.96 ± .05	6.94 ± .03
Cl	.227				7.69 ± .03	
Br	.232		6.95 ± .04	7.01 ± .04		7.77 ± .03
NO₂	1.270			9.83 ± .07		

giving information on this point, and the *pK* of this compound confirms the appropriateness of σ^--constants for the Y-substituents. Hence eq. 2 should be rewritten

$$\log (K_{oy}/K_{oo}) = \sigma_y^{-}\rho_y \qquad (2')$$

The lack of further compounds capable of testing the applicability of σ^--values is in part predicated by the fact that most substituents for which σ and σ^- differ are themselves basic centers (*e.g.*, COOH and COR) of about the same basity as the azoxy group itself, or are unstable in acidic solution (*e.g.*, CN and COOR, which may be hydrolyzed). Also, compounds with these strongly electron-withdrawing substituents tend to be very weak bases and were avoided because the very strongly acidic solutions required in these cases produced considerable experimental difficulties, as discussed under preparation of solutions. Some additional cases are now under investigation.

Examination of Table III shows that there is a number of other series permitting application of the simple Hammett equation. These series are those in which either X remains fixed (CH_3 or Br) while Y is varied, or Y remains fixed (again CH_3 or Br) while X is varied. This corresponds, respectively, to vertical and horizontal rows of Table III. If K_{xy} is the equilibrium constant for the 4-X-4′-Y-derivative, eq. 1 and 2 can be generalized to

$$\log (K_{xy}/K_{oy}) = \sigma_x\rho_x^y \qquad (1'')$$

$$\log (K_{xy}/K_{xo}) = \sigma_y\rho_y^x \qquad (2'')$$

where ρ_x^y is the reaction constant which measures the effect on the equilibrium of varying X with Y constant, and conversely ρ_y^x measures the effect of varying Y with X remaining fixed. Admittedly the application of the Hammett equation to series of three compounds leaves much to be desired, but this is the best that can be done with the available data. The application of eq. 1″ and 2″ to the data of Table III is shown in Table IV and in Fig. 1. Examination of these results shows that differences between the various ρ_x^y and ρ_y^x appear to occur; they appear to parallel roughly the σ-values of Y and X, respectively, and in this way are similar to the corresponding σ-values in the azobenzene derivatives.[4b] However, the experimental material available at this time is insufficient to demonstrate unequivocally this conclusion; the standard deviations of the ρ-values are so large that the observed differences, generally, are not significant. Examination of Table IV also shows that differences between ρ_x^y and ρ_y^x are small, except for X and Y = H. This fact is at first surprising since the substituent Y is at a greater distance from the presumed basic center, the O-atom, than X. The explanation probably lies in the greater importance of resonance effects from Y, and one might speculate that a separation of inductive and resonance effects, following Taft,[13] would lead to an inequality $\rho_{\mathrm{I}}{}_x^y > \rho_{\mathrm{I}}{}_y^x$, which is balanced by an inequality of resonance effects in the opposite direction.

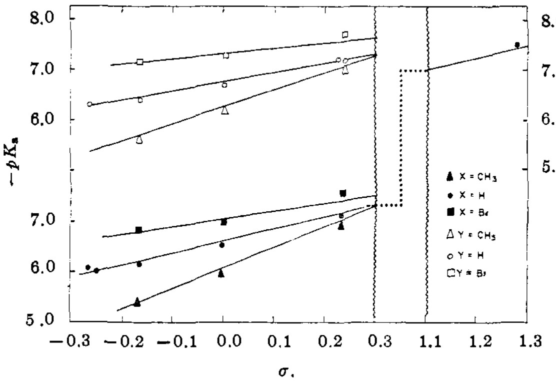


Fig. 1.—Plot of $-pK$'s *vs.* σ.

A more unified treatment of substituent effects in all the azoxy compounds now seems desirable. A number of possibilities suggest themselves. The simplest is suggested by our inability to find large differences between the various ρ_x^y and ρ_y^x. Assuming all of these values equal leads to

$$\log (K_{xy}/K_{oo}) = (\sigma_x + \sigma_y^{-})\rho \qquad (3)$$

The results obtained by application of eq. 3 are included in Table IV, and are seen to represent the data with good accuracy.

TABLE IV

REACTION CONSTANTS FOR THE DISSOCIATION OF THE CONJUGATE ACIDS OF SUBSTITUTED AZOXYBENZENES

	Equation 1			Equation 2			
	X = H	X = CH₃	X = Br	Y = H	Y = CH₃	Y = Br	Eq. 3
ρ	2.508	2.868	2.247	1.735	2.857	2.113	2.491
r	0.995	0.997	0.924	0.984	0.999	0.932	0.999
s	.050	.014	.260	.083	.020	.233	.166
s_ρ	.038	.036	.912	.182	.071	.816	.099
log K°	6.57	6.12	7.16	6.53	6.06	7.11	6.57
n	6	3	3	5	3	3	16

It had previously been found that ρ-values are frequently independent of substituents in the side chain.[11h] This statement is equivalent to saying that all the ρ_x^y of eq. 1″ are equal, since this equa-

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[13] R. W. Taft, Jr., "Steric Effects in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1956.

tion considers —N(O)=NC$_6$H$_4$Y-*p* as the side chain, and similarly that all the ρ_y^x are equal, and implies the equation

$$\log (K_{xy}/K_{oo}) = \sigma_x\rho_x + \sigma_y^-\rho_y \qquad (4)$$

Application of eq. 4 leads to $\rho_y = 2.46 \pm 0.12$, $\rho_x = 2.25 \pm 0.26$, $R = 0.988$, $s = 0.169$ with $n = 16$. Inspection shows that ρ_x and ρ_y are not significantly different, and hence there appears little to recommend eq. 4 over eq. 3. However a much more sensitive test can be devised, based on the analysis of variance.[14] This procedure is particularly attractive here because replicate determinations are available, and provide an independent estimate of error, so that it is not necessary to use the deviations from the best equation as this estimate, as was done in previous work.[14]

For each of the compounds at least three determinations of the *pK* were available at each of two wave lengths, representing substantially the major absorption bands of the free base and of the conjugate acid. Only for the 4-nitro compound, data had been obtained at only one wave length, and an appropriate adjustment for the missing data was made. Where more than three replicate data were available for a given compound and wave length, three were selected at random. In this way, a table of 92 determinations was constructed. Of the total of 95 degrees of freedom, 3 were sacrificed because of missing data, 15 represented compound differences, one the wave length differences, and 14 the compound–wave length interactions. The remaining 62 degrees of freedom are directly ascribable to experimental error. The fifteen degrees of freedom for compound differences can be broken up in several ways: 2 due to the regression expressed by eq. 4 and 13 for deviations from this regression; or one due to the regression of eq. 3 and 14 for the deviations from eq. 3. The one degree of freedom which is the difference between eq. 4 and 3 represents the improvement obtained by use of the more complicated equation.

The results of the analysis are given in Table V. Surprisingly, the difference between the two wave lengths is significant, although only barely and only at the 95% level; encouragingly, the wave length compound interactions are completely without significance. As expected, the compound differences are highly significant, accounting for well over 99% of the total variance. Again as expected, but gratifying to be confirmed, some 98% of the variance is accounted for by the regression, using either of the equations. The approximate nature of the Hammett equation is confirmed by the high significance of the deviations from even the best equation. Finally, however, the improvement of eq. 4 over eq. 3 is seen to be significant, even at the 99% level; still it accounts for less than 0.1% of the total variance. Thus, one may conclude that eq. 4 is superior to eq. 3, but not greatly superior.

TABLE V

ANALYSIS OF VARIANCE OF *pK* VALUES OF AZOXYBENZENE

Source	D.f.	Sum of squares	Mean squares	F^a
Total	92	100.58935	.....	....
Between wave length	1	0.01126	0.01126	4.83*
Between compounds	15	100.39995	6.69330	2872**
Due to eq. 4	2	98.04616	49.02308	>1000**
Due to eq. 3	1	97.96146	97.96146	>1000**
Improvement eq. 4 over eq. 3	1	0.08470	0.08470	36.4**
Devn. from eq. 4	13	2.35379	.18106	77.7**
Wave lengths and cmpds. interaction	14	0.03344	.00223	1
Error	62	0.14470	.00233	....

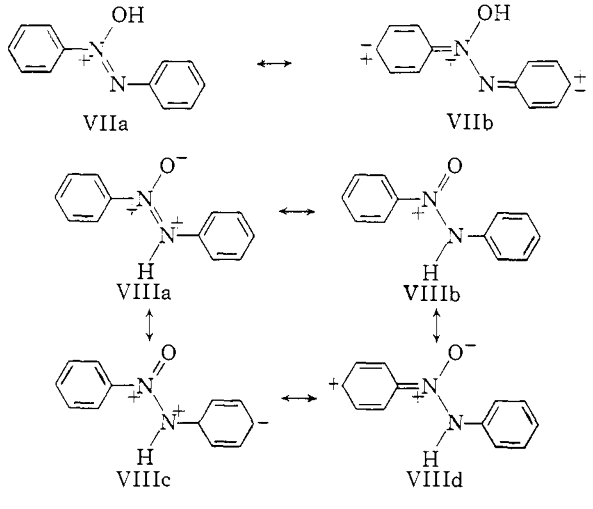
[a] Significance at the 95% level is indicated by one asterisk, at the 99% level by two.

A final treatment of the data suggests itself, based on the above observaion that the ρ_x^y seemed to parallel σ_y and the ρ_y^x, σ_x, and the consequent need for an interaction term as emphasized by Miller.[15] This leads to the equation

$$\log (K_{xy}/K_{oo}) = \sigma_x\rho_x + \sigma_y^-\rho_y + \sigma_x\sigma_y^-\rho_{xy} \qquad (5)$$

Inclusion of the last term was tested in the analysis of variance procedure; now three degrees of freedom are represented by eq. 5, and the difference to the two d.f. for eq. 4 measures the improvement, which was found to be completely non-significant. However, it remains possible that with a greatly expanded body of data, even the last term of eq. 5 could become significant.

It finally remains to inquire where the proton in the conjugate acids of azoxybenzene is bound. The two most likely structures for the conjugate acid appear to be VII and VIII. Although both VIIa and VIIIb are structures not involving separation of charge, it would appear that the energy of VIIIb should be high, because the two rings are conjugated only through high energy structures. Compounds VIIIa and c, with adjacent positive charges, obviously have very high energy and hence are unlikely to make an appreciable contribution to the ground state. VIIId might stabilize VIII to about the same extent as one of the two structures VIIb stabilizes VII. Thus it seems likely that VII represents the structure of the conjugate acid, as assumed above. This con-


VIIa VIIb
VIIIa VIIIb
VIIIc VIIId

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[14] H. H. Jaffé, *J. Org. Chem.*, **23**, 874 (1958).

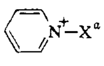
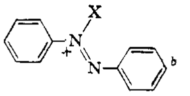
[15] S. I. Miller and P. K. Yonan, *J. Am. Chem. Soc.*, **79**, 5931 (1957); S. I. Miller, *ibid.*, **81**, 101 (1959).

clusion is consistent with the interpretations of the substituent effects given above and with the spectroscopic data to be reported elsewhere, although neither of these is capable of making a distinction between VII and VIII.

The difference in basicities of pyridine and its N-oxide is compared in Table VI with the difference between azobenzene and azoxybenzene, the latter of which may well be considered as an N-oxide of azobenzene. In both series the N-oxides are weaker bases by nearly the same amounts. This observation seems to suggest that the structure of the conjugate acids of the N-oxides is quite similar, and there seems to be no reason to doubt that the conjugate acid of pyridine N-oxide is N-hydroxypyridinium ion.[16] Consequently it seems safe to conclude that azoxybenzenes are protonated at the oxygen atom.

TABLE VI

COMPARISON OF *pK* BETWEEN PYRIDINE, AND ITS N-OXIDE, AND AZO- AND AZOXYBENZENE

X	[a]	[b]	Difference
H	5.29	−2.90[c]	8.19
OH	0.79	−6.45	7.24
Difference	4.50	3.55	

[a] In H_2O; *cf.* ref. 16, 5b. [b] In 20% EtOH. [c] Ref. 4b.

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[16] H. H. Jaffé, *J. Am. Chem. Soc.*, **79**, 4445 (1955).

[CONTRIBUTION FROM THE ESSO RESEARCH AND ENGINEERING CO., LINDEN, N. J.]

Ionic Reactions Occurring During Sulfuric Acid Catalyzed Alkylation. I. Alkylation of Isobutane with Butenes

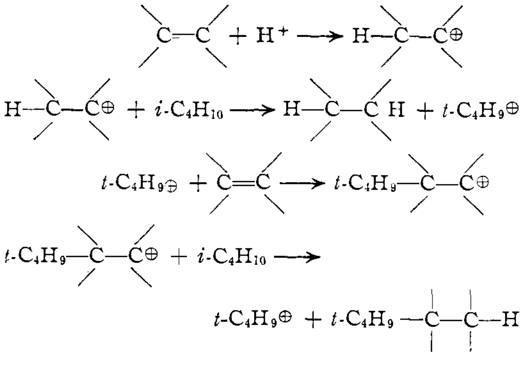
BY J. E. HOFMANN AND A. SCHRIESHEIM

RECEIVED AUGUST 18, 1961

The sulfuric acid catalyzed alkylation between isobutane and butene-1, butene-2 and isobutylene was studied in continuous flow equipment. Product analyses were obtained as a function of time, and profound changes were found in hydrocarbon distribution. Initially, yields were low, but selectivity to trimethylpentanes was high. This was followed by an intermediate period of increasing yield but markedly reduced selectivity to trimethylpentanes. Finally, equilibrium experimental conditions were reached. Selectivity to trimethylpentane was again high and yields approached the theoretical. The results are interpreted by assuming the buildup of an isobutane solutizer or active hydride transfer agent in the acid phase.

Introduction

The acid catalyzed alkylation of olefins with isoparaffins was first described by Ipatieff.[1] This reaction is induced by a wide variety of catalysts, and it has been comprehensively reviewed by Kennedy[2] and Schmerling.[3] A careful study of the literature, however, shows that there is very little specific information concerning the role of the catalyst. Thus, it has been generally accepted that in protonic acids, as sulfuric, the olefin is protonated (step 1) to yield a carbonium ion that undergoes a hydride exchange reaction[4,5] (step 2) with a molecule of isobutane to generate the *t*-butyl cation. This cation then reacts with more olefin to form the alkylate ion (step 3), which may then undergo a second hydride transfer reaction to regenerate the chain-carrying *t*-butyl ion and produce the alkylate molecule.



$$\text{>C=C<} + H^+ \longrightarrow H\text{—C—C}^{\oplus} \qquad (1)$$

$$H\text{—C—C}^{\oplus} + i\text{-}C_4H_{10} \longrightarrow H\text{—C—C}H + t\text{-}C_4H_9^{\oplus} \qquad (2)$$

$$t\text{-}C_4H_9^{\oplus} + \text{C=C} \longrightarrow t\text{-}C_4H_9\text{—C—C}^{\oplus} \qquad (3)$$

$$t\text{-}C_4H_9\text{—C—C}^{\oplus} + i\text{-}C_4H_{10} \longrightarrow t\text{-}C_4H_9^{\oplus} + t\text{-}C_4H_9\text{—C—C—H} \qquad (4)$$

In a classic series of papers, Beeck, *et al.*,[6] showed that hydride transfer does, indeed, occur on the tertiary C–H bond of isobutane. The results of these investigations when coupled with previous research[2,3] tended to support the assumption that the acid serves merely to initiate the reaction by protonation of the olefin and to provide an ionic media for the reaction to take place. Certain inconsistencies in this interpretation developed during our general research program on acid catalysis,[7]

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[1] V. N. Ipatieff, "Catalytic Reactions of High Pressures and Temperatures," The Macmillan Co., New York, N. Y., 1936, pp. 673–701.

[2] R. M. Kennedy, "Catalysts," Vol. 6, Reinhold Publ. Corp., New York, N. Y., 1958, pp. 1–41.

[3] L. Schmerling, "The Chemistry of Petroleum Hydrocarbons," Vol. 3, Reinhold Publ. Corp., New York, N. Y., 1955, pp. 363–408.

[4] P. D. Bartlett, F. E. Condon and A. Schneider, *J. Am. Chem. Soc.*, **66**, 1531 (1944).

[5] N. C. Deno, H. J. Peterson and G. S. Saines, *Chem. Revs.*, **60**, No. 1, 7 (1960).

[6] O. Beeck, J. W. Otvos, D. P. Stevenson and C. D. Wagner, *J. Chem. Phys.*, **17**, 418 (1949); *J. Am. Chem. Soc.*, **73**, 5741 (1951); **74**, 3299 (1952).

[7] G. M. Kramer and A. Schriesheim, *J. Phys. Chem.*, **66**, in press (1962). Unpublished work from this Laboratory by Dr. G. M. Kramer indicated rather clearly that alkylate is not formed when fresh sulfuric acid is contacted with isobutane and isobutylene for short contact times. This work was carried out by mixing hydrocarbon and fresh acid in a mixing tee and then rapidly quenching the emulsion with caustic. Analysis of the low boiling fraction indicated complete conversion of the olefin but no significant quantity of higher boiling saturated hydrocarbons could be found. A small yield of 2,4,4-trimethylpentene-1 was detected and also a fairly large amount of unsaturated material boiling in the C_{12} and higher range was formed. Clearly, this was the result of olefin dimer and trimerization with no significant amount of hydride transfer between isobutane and the higher molecular weight ionic fragments.