

[CONTRIBUTION FROM KOPPERS CO., INC., MONOMER FELLOWSHIP AT MELLON INSTITUTE]

Steric Hindrance. II. The Rates of Dehalogenation of Methyl- and Dimethylstyrene Dibromides¹

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The ultraviolet absorption maxima and molar refractions of positional isomeric methyl- and dimethylstyrenes are consistent with the concepts of steric hindrance, resonance and induction. For example, the absorption maxima and exaltations of the methylstyrenes stand in the order *para* > *meta* > *ortho*. Among the dimethylstyrenes, the 2,6-isomer absorbs at the shortest wave length, owing to steric inhibition of resonance, and the 3,5-isomer absorbs at the longest wave length, because of first-order hyperconjugation of the methyl groups. The rates of dehalogenation of the styrene dibromides in the presence of potassium iodide reveal the interplay of resonance, inductive and steric effects. The steric effects are predominant. The dibromide of *p*-methylstyrene dehalogenates faster than the dibromide of 3,5-dimethylstyrene, which dehalogenates faster than the dibromide of *m*-methylstyrene. *o*-Methylstyrene dibromide dehalogenates much more rapidly than *p*-methylstyrene dibromide as the result of steric acceleration. The data presented in this paper suggest an S_N2 mechanism as the rate-determining step in the dehalogenation of methyl-substituted styrene dibromides by means of potassium iodide.

In general this contribution attempts to clarify the resonance, inductive and steric effects in several methylstyrenes in terms of ultraviolet absorption spectra, molar refractions and the kinetics of the dehalogenation of the styrene dibromides.

Since any difference in the energy of the "first excited state" (ionic state) with respect to that of the ground state becomes evident in the ultraviolet absorption, we have examined the spectra of styrene, α -methylstyrene, the three methylstyrenes and four of the dimethylstyrenes (Table I). It is assumed in this paper that the ground state energies of these isomeric styrenes are essentially the same and that the effect of alkyl substitution on the absorption spectra is due mainly to preferential stabilization of the ionic state.²

The spectra of the methylstyrenes show the *para*-derivative absorbing farther toward the red than the *meta*-derivative. This finding is to be expected because the combined resonance and inductive effects of the *p*-methyl group decrease the energy difference between the ground state and the "first excited state" more than the inductive effect of the *m*-methyl group. On the other hand, steric hindrance to coplanarity in the "first excited state" of *o*-methylstyrene, in spite of the inductive and resonance effects, decreases the resonance energy with the result that the wave length of maximum absorption is less than that of styrene.

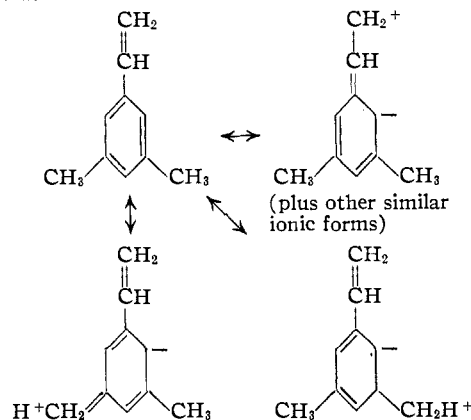
α -Methylstyrene absorbs farther in the ultraviolet than styrene owing to hindrance between the α -methyl group and the *o*-hydrogens. Although the steric hindrance to coplanarity should be about the same for a styrene substituted with an *o*-methyl group as one with an α -methyl group, *o*-methylstyrene absorbs at a longer wave length (246 $m\mu$) than does α -methylstyrene (243 $m\mu$). This bathochromic shift of *o*-methylstyrene may be explained in terms of the effect of hyperconjugation of the *o*-methyl group.³

The dimethylstyrenes present an interesting correlation of spectra with structure. The inductive effect of the *m*-methyl group in 2,5-dimethylstyrene

decreases the energy difference between the ground state and the ionic state relative to *o*-methylstyrene causing a bathochromic shift to 247 $m\mu$. With regard to 2,4-dimethylstyrene, the increased resonance energy caused by the combined inductive and resonance effects of the *p*-methyl group has been minimized by the decreased resonance energy owing to the steric hindrance to coplanarity imposed by the *o*-methyl group. Consequently, 2,4-dimethylstyrene has an absorption maximum (251 $m\mu$) intermediate between that of *o*-methylstyrene (246 $m\mu$) and *p*-methylstyrene (253 $m\mu$).

Of the styrenes reported in this paper, 2,6-dimethylstyrene absorbs at the shortest wave length (238 $m\mu$) and 3,5-dimethylstyrene absorbs at the longest wave length (254 $m\mu$). The short wave length absorption of 2,6-dimethylstyrene results from steric inhibition of resonance by diortho-substitution⁴ whereas the bathochromic shift of 3,5-dimethylstyrene is attributable in part to hyperconjugation of the methyl groups.

Although *m*-substitution is not usually thought of as contributing to resonance, we suggest the following ionic states, involving first-order hyperconjugation of the methyl groups, to account for this anomaly. These ionic states cause the resonance energy of the mesomeric system to be considerably increased with the result that 3,5-dimethylstyrene absorbs farther toward the visible than the other isomers.



Mulliken⁵ has indicated that the molar refraction

(1) Presented before the 127th Meeting of the American Chemical Society, Cincinnati, Ohio, March 29, 1955.

(2) W. C. Price, *Chem. Rev.*, **41**, 257 (1947); W. H. Rodebush, *ibid.*, **41**, 317 (1947).

(3) M. T. O'Shaughnessy and W. H. Rodebush, *THIS JOURNAL*, **62**, 2906 (1940); R. N. Jones, *ibid.*, **67**, 2127 (1945); Y. Hirschberg, *ibid.*, **71**, 3241 (1949).

(4) L. H. Schwartzman and B. B. Corson, *ibid.*, **76**, 711 (1954).

(5) R. S. Mulliken, *J. Chem. Phys.*, **7**, 356 (1939).

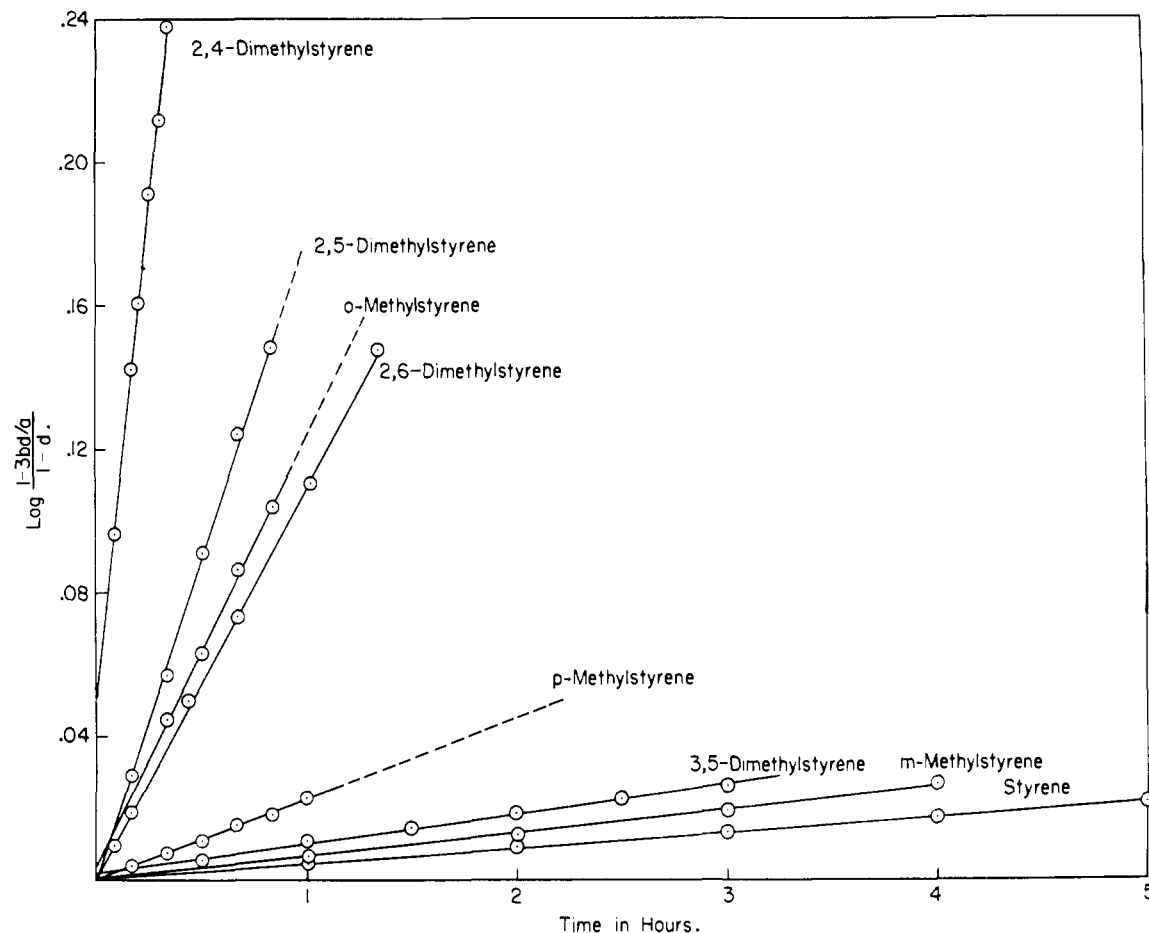
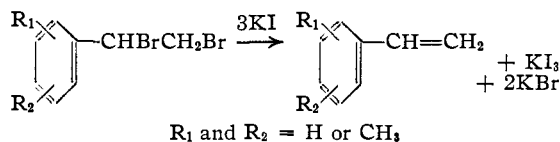


Fig. 1.—Relative rates of dehalogenation of the corresponding styrene dibromides at 39.6°.

tions of positional isomeric alkylstyrenes should roughly parallel the ultraviolet absorption maxima. In other words, exaltation should be a measure of change in resonance energy. With methyl- and dimethylstyrenes the effect of first-order hyperconjugation of the methyl groups is an important element in molecular exaltations and absorption maxima. The molar refractions of the methylstyrenes stand in the order *para* > *meta* > *ortho*, and the ultraviolet absorption maxima are in the same order (Table I). The dimethylstyrenes show identical parallelism (Table I).

The rates of dehalogenation of the (α,β -dibromoethyl)-benzenes were measured so as to find the relationship of structure with reactivity. The experimental method was essentially that employed by previous workers.⁶ Aliquot samples of dibromide plus potassium iodide were allowed to react at 39.6° for different periods of time, and the liberated iodine was titrated as a measure of the rate of reac-



(6) R. T. Dillon, W. G. Young and H. J. Lucas, *THIS JOURNAL*, **52**, 1953 (1930); R. T. Dillon, *ibid.*, **54**, 952 (1932); S. Winstein, D. Pressman and W. G. Young, *ibid.*, **61**, 1645 (1939); D. Pressman and W. G. Young, *ibid.*, **66**, 705 (1944).

tion. The ionic strength was kept constant by always using the same concentration of dibromide and potassium iodide.

The following conclusions can be drawn from the kinetic data in Table II and Fig. 1. (1) The reaction of methyl- and dimethylstyrene dibromides with potassium iodide (dibromide/iodide molar ratio = 1/10) in 99% methanol at 39.6° follows second-order kinetics, according to the equation

$$k_{\text{obsd}} = \frac{2.303}{t(a-3b)} \log \frac{1-3bd/a}{1-d}$$

where a and b = initial concentrations of potassium iodide and dibromide, respectively (moles/liter at 20°), and d = fraction of total dibromide reacted at time t (in hours).

(2) Although it has been assumed⁷ that the rate-determining step in debromination is the attack on the α -position, the possibility exists that the β -position may be attacked concurrently or exclusively. The inductive, resonance and the steric effects found in this study definitely suggest that the α -position is the major reaction center. Taylor,⁸ in a study of the reaction of α - and β -phenethyl bromides with potassium hydroxide in absolute ethanol, found that the reaction rate was second order, and that the SN2 reaction proceeded about four

(7) T. L. Davies and R. Heggie, *J. Org. Chem.*, **2**, 470 (1937).

(8) W. Taylor, *J. Chem. Soc.*, 343 (1937).

times as fast with the α -compound as with the β -compound.

TABLE I
ABSORPTION MAXIMA AND MOLAR REFRACTIONS OF ISOMERIC ALKYLSTYRENES

Styrene	n_D^{20}	d_{20}^{20}	Molar refraction	$\lambda_{max}, m\mu^a$
Styrene	1.5469	0.9060	36.45	248
α -Methyl-	1.5386	.9106	40.63	243
<i>o</i> -Methyl-	1.5437	.9145	41.02	246
<i>m</i> -Methyl-	1.5410	.9028	41.13	251
<i>p</i> -Methyl-	1.5420	.8976	41.44	253
2,6-Dimethyl-	1.5314	.9094	45.00	238
2,5-Dimethyl-	1.5395	.9048	45.78	247
2,4-Dimethyl-	1.5426	.9066	45.94	251
3,5-Dimethyl-	1.5382	.8950	46.22	254

^a All ultraviolet spectra were measured in cyclohexane solution with a Cary recording spectrophotometer.

TABLE II
DEHALOGENATION OF STYRENE DIBROMIDES AT 39.6°

Styrene, dibromide	Mole/liter	KI, mole/liter	$k_{obsd.}$, liter-mole ⁻¹ hr. ⁻¹	$k_{cor.}^a$, liter-mole ⁻¹ hr. ⁻¹
Styrene ^b	0.0255	0.2521	0.057	0.058
<i>o</i> -Methyl-	.0253	.2504	1.703	1.740
<i>m</i> -Methyl-	.0247	.2516	0.085	0.087
<i>p</i> -Methyl-	.0253	.2504	0.293	0.299
2,6-Dimethyl-	.0249	.2502	1.443	1.475
2,5-Dimethyl-	.0263	.2511	2.306	2.357
2,4-Dimethyl-	.0260	.2505	7.482	7.647
3,5-Dimethyl-	.0251	.2499	0.119	0.122

^a Corrected for solvent expansion from 20 to 39.6°. ^b k_{obsd} at 75.00 \pm 0.02° = 1.641; D. Pressman and W. G. Young⁸ report k_{obsd} at 74.59° = 1.643.

and twenty times as fast as the *m*-methyl derivative (Fig. 1). However, resonance and inductive effects are still evident in that the rate of dehalogenation decreases from 2,4-dimethylstyrene dibromide to 2,5-dimethylstyrene dibromide to *o*-methylstyrene dibromide (Fig. 1).

(5) Whereas the introduction of a single *o*-methyl group in any of the styrene dibromides results in a steric acceleration of the rates of dehalogenation, the introduction of a second *o*-methyl group (*i. e.*, 2,6-dimethylstyrene dibromide) results in a steric hindrance which leads to a deceleration of the rate of dehalogenation (Fig. 1).

A possible explanation may be that the α -position in 2,6-dimethylstyrene dibromide is more hindered than the α -position in *o*-methylstyrene dibromide, and that the rate-determining step in the dehalogenation of the dibromide of 2,6-dimethylstyrene involves an attack on the β -position.

(6) The mechanism proposed by Winstein, Pressman and Young⁶ for the dehalogenation of vicinal dibromides is one in which a negative iodide ion removes a positive bromine atom with concurrent backside attack of the electron pair from the displaced bromine onto the adjacent carbon, thereby producing the resulting olefin with one stereochemical inversion. Although this mechanism accounts for the stereochemical result of *trans*-elimination leading to *cis*- or *trans*-olefins, our data are also consistent with the bimolecular replacement mechanism as has been proposed for the dehalogenation of 1,2-dibromoethane, 1,2-dibromopropane and 1,2-dibromobutane.⁹

We believe the rate-determining step in the dehalogenation of methyl-substituted styrene dibro-

TABLE III
PREPARATION OF METHYL- AND DIMETHYLSTYRENES

Styrene	Method of prepn.	Yield, %	°C.	B.p. Mm.	M.p., °C.	Purity (mole %)	Dibromide ^a	
							M.p., °C.	Bromine, % Calcd. Found
Styrene ^b	60	40	-30.77	99.7	72-73	60.5 60.5
<i>o</i> -Methyl- ^c	A	..	67-68	20	-68.39	99.5	i	57.5 56.8
<i>m</i> -Methyl- ^d	63-64	20	>95 ^h	48.5-49.0	57.5 57.1
<i>p</i> -Methyl- ^e	B	..	81	41	-33.85	99.7	44.0-44.5	57.5 57.4
2,4-Dimethyl- ^f	B	84	57	4	-64.32	99.3	i	54.7 54.3
2,5-Dimethyl- ^f	A	93	68-69	10	-35.41	99.4	64.0-64.5	54.7 54.4
2,6-Dimethyl- ^g	A	75	65-66	10	-38.65	99.4	48-50	54.7 54.4
3,5-Dimethyl- ^g	..	62	56	4	-60.19	99.5	90.5-91.0	54.7 54.4

^a The dibromides were prepared by bromination of the corresponding styrenes in carbon tetrachloride at -50°. ^b Koppers Co. styrene. ^c Prepared by Mr. W. J. Heintzelman by method A according to Hershberg.³ ^d Prepared by Mr. W. J. Heintzelman by the dehydrogenation of *m*-ethyltoluene over chromia-alumina catalyst at 650°, 1 second contact time with a 10/1 steam-hydrocarbon mole ratio. ^e Prepared by Dr. F. J. Pavlik by method B according to F. R. Buck, K. F. Coles, G. T. Kennedy and F. Morton, *J. Chem. Soc.*, 2377 (1949). ^f C. S. Marvel, J. H. Saunders and C. B. Overberger, *THIS JOURNAL*, 68, 1085 (1946). ^g Mesitylene was converted to mesityl bromide (b.p. 73-76° (1.4 mm.), m.p. 37-38°, 66% yield) with N-bromosuccinimide which in turn was converted to 3,5-dimethylphenylacetic acid (91% yield) *via* the nitrile. Lithium aluminum hydride reduction of the acid gave 99.5% yield of β -(3,5-dimethyl)-phenethyl alcohol (b.p. 128-129° (15 mm.)) which was dehydrated over Al₂O₃ at 350° under 11 mm. of nitrogen to give 3,5-dimethylstyrene. ^h Purity determined by infrared analysis; all other styrenes analyzed by cryoscopic method. ⁱ B.p. 98.5-99.5° (1 mm.), n_D^{20} 1.6041, d_{20}^{20} 1.6878. ^j Crystallized twice at -70° and distilled; b.p. 111° (1.2 mm.).

(3) The inductive and resonance effects are clearly evident; *e.g.*, *p*-methylstyrene dibromide dehalogenates faster than 3,5-dimethylstyrene dibromide, which in turn reacts faster than the dibromide of *m*-methylstyrene (Fig. 1).

(4) Steric effects influence the rate of dehalogenation more than inductive and resonance effects. For example, *o*-methylstyrene dibromide dehalogenates six times as fast as the *p*-methyl derivatives

by potassium iodide in 99% methanol to be a nucleophilic attack (S_N2) of iodide ion on the α -carbon atom followed by a rapid elimination to form the corresponding styrenes. In this manner, the acceleration of the rates of dehalogenation of the styrene dibromides owing to the inductive and

(9) J. Hine and W. H. Brader, Jr., *THIS JOURNAL*, 77, 361 (1955); H. L. Goering and H. H. Espy, *ibid.*, 77, 5023 (1955); W. M. Schubert, H. Steady and B. S. Rabinovitch, *ibid.*, 77, 5755 (1955).

resonance effects of the methyl group becomes explicable.

Several workers have shown that benzyl halides with nucleophilic reagents in solvents of low dielectric constant can react by a bimolecular (S_N2) mechanism and, moreover, that the *p*-methyl group increases the rate of this reaction over that of the unsubstituted compound.¹⁰

Franzen and Rosenberg¹¹ reported that benzyl chlorides, substituted in the aromatic ring, react with sodium ethoxide in absolute ethanol according to second-order kinetics and that the order of reactivity is *o*-CH₃ > *p*-CH₃ > *m*-CH₃ > H. This is the same order observed in this study.

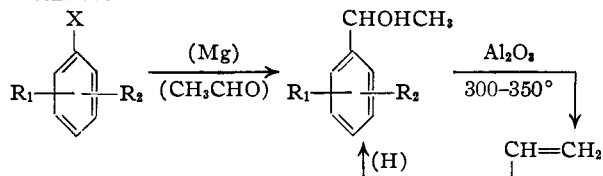
(10) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, p. 327.

(11) H. Franzen and I. Rosenberg, *J. prakt. Chem.*, [2] **101**, 333 (1920).

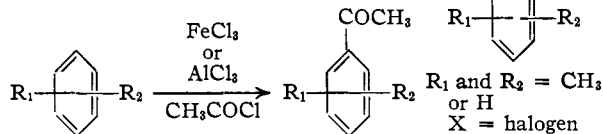
Experimental

For most of the styrenes reported in this paper, two general methods of preparation were used.

Method A



Method B



PITTSBURGH 13, PENNA.

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENTS OF THE UNIVERSITY OF MICHIGAN AND TULANE UNIVERSITY]

Acid-catalyzed Reactions of Aliphatic Azides¹

BY J. H. BOYER, F. C. CANTER, J. HAMER AND R. K. PUTNEY

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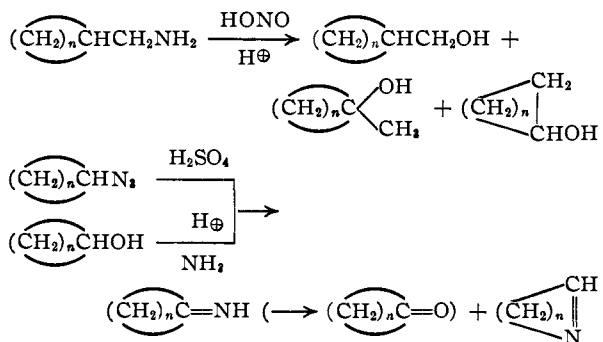
Ring expansion accounted for the major reaction of the alicyclic azides of the common rings in sulfuric acid. Migration of the *n*-propyl group from carbon to nitrogen as well as the formation of butyraldime accounted for the products obtained from *n*-butyl azide. Similar treatment of *n*-hexyl and *n*-dodecyl azides in sulfuric acid, however, afforded nearly quantitative conversion to the corresponding aldimines. In contrast, triphenylmethyl azide underwent quantitative hydrolysis into triphenylcarbinol. Propylene and trimethylene azidohydrins with aromatic aldehydes in sulfuric acid were transformed into oxazolines and dihydrooxazines, respectively.

Whereas the normal action of strong acids upon aliphatic azides promotes the formation of imines, the presence of aldehydes was observed to bring about the formation of other products.² The work reported here was designed to obtain additional information on certain factors which control the formation of imines or Schiff bases and to learn more of the limitations of the reaction with aldehydes.

Benzyl,^{3a} ethyl^{3b} and now *n*-butyl azides have been observed to undergo acid-catalyzed transformation into aldimines by either hydrogen or alkyl migration. In agreement with the expected increased difficulty for larger alkyl groups to migrate from carbon to nitrogen, aldimines (isolated as corresponding aldehydes) were obtained from similar treatment of *n*-hexyl and *n*-dodecyl azides in which only hydrogen migration was involved. Quantitative conversion of triphenylmethyl azide in concentrated sulfuric acid into triphenylcarbinol provided one of the rare examples of acid hydrolysis of an alkyl azide.⁴

The predominance of ring expansion over ring-size retention for alicyclic azides of the common rings is reminiscent of the Demjanow ring expansion⁵

of cycloalkylmethylamines on the one hand and parallels acid-catalyzed reactions of hydrogen azide upon alcohols⁶ on the other. Similar results were obtained from the azides with stannic chloride and anhydrous hydrogen chloride in benzene; however, they were more resistant to attack by phosphoric acid.



Attempts to isolate and identify products resulting from possible reactions between benzaldehyde and either linear or cyclic aliphatic azides were unsuccessful. Apparently *N*-substituted benzamides failed to occur or did so in only trace amounts (compare the formation of *N*- β -phenylethylbenzamide from β -phenylethyl azide and benzaldehyde). The formation of hexahydro-1,3,5-triazine (isolated as the tribenzoyl derivative) in the treatment

(1) The financial support for this work came from the Office of Ordnance Research, U. S. Army under Contract Nos. DA-01-009-ORD-428, DA-01-009-ORD-331, DA-20-018-ORD-12763 and DA-20-018-ORD-11814. The work on alicyclic azides was included in a paper presented at the XIVth International Congress of Pure and Applied Chemistry, Zurich, Switzerland, July 21 to 27, 1955.

(2) J. H. Boyer and J. Hamer, *THIS JOURNAL*, **77**, 951 (1955).

(3) (a) T. Curtius and G. Ehrhart, *Ber.*, **55**, 1559 (1922); (b) K. W. Sherck, A. G. Haupt and A. W. Browne, *THIS JOURNAL*, **62**, 329 (1940).

(4) J. H. Boyer and F. C. Canter, *Chem. Revs.*, **54**, 26 (1954).

(5) P. A. S. Smith, D. R. Baer and S. N. Ege, *THIS JOURNAL*, **76**, 4564 (1954).

(6) J. H. Boyer and F. C. Canter, *ibid.*, **77**, 3287 (1955).