

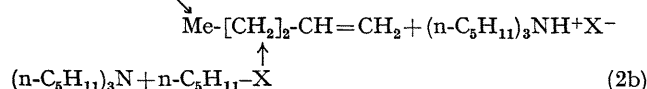
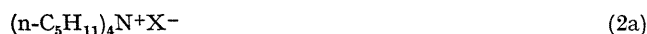
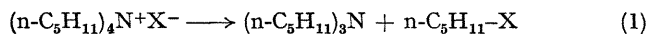
## Nucleophilicity of Halide Ions in Molten Quaternary Ammonium Salts

By JOHN E. GORDON\* and POTHEN VARUGHESE

(Department of Chemistry, Kent State University, Kent, Ohio 44242)

**Summary** The relative rates of nucleophilic displacement by halide ions from tetra-*n*-pentylammonium cations in the molten tetrapentylammonium salts at 180° (Cl<sup>-</sup>: Br<sup>-</sup>: I<sup>-</sup> = 620:7.7:1) reflect the enhanced nucleophilicity expected for unsolvated, unassociated halide ions.

In molten quaternary ammonium salt media, where deactivation by ion solvation and ion association<sup>1</sup> are absent,<sup>2</sup> halide ions should show a nucleophilic reactivity in the order: F<sup>-</sup> > Cl<sup>-</sup> > Br<sup>-</sup> > I<sup>-</sup>. This proposition has not been rigorously tested. The reverse Menschutkin reaction (1) is qualitatively more rapid for X = Br than for X = I in studies in sealed ampoules,<sup>3</sup> but the reaction is accompanied by formation of olefin [equation (2)]. It is



known that at least part of this olefin is produced *via* equation (2b) under these conditions,<sup>3</sup> but a direct *E2* process with X<sup>-</sup> as base [equation (2a)] has not been ruled out. Pyrolysis of some alkaloid methohalides under the

high-vacuum conditions obtaining in the ionization chamber of a mass spectrometer gives predominantly elimination;<sup>4</sup> since secondary RX-R<sub>3</sub>N reaction is unlikely under these conditions, the *E2* path (2a) must be the source.

We have now established conditions (180°; 10<sup>-3</sup> Torr) under which the tetra-*n*-pentylammonium halides decompose entirely *via* equation (1), allowing determination of the relative rates of displacement by competition experiments. The results in the Table yield the relative rates: Cl<sup>-</sup>: Br<sup>-</sup>: I<sup>-</sup> = 620:7.7:1, in accord with the theory of medium effects on X<sup>-</sup> nucleophilicity which identifies the inversion of the nucleophilicity order I<sup>-</sup> > Br<sup>-</sup> > Cl<sup>-</sup>, observed in hydroxylic solvents, to Cl<sup>-</sup> > Br<sup>-</sup> > I<sup>-</sup> in dipolar aprotic solvents with the structural change: X<sup>-</sup> ··· H-O-R → X<sup>-</sup>.<sup>1,5,6</sup> The poorly solvated X<sup>-</sup> in dipolar aprotic solvents are more reactive than their X<sup>-</sup> ··· H-O-R counterparts by factors ranging from 10<sup>4</sup> for I<sup>-</sup> to 10<sup>7</sup> for the more strongly solvated Cl<sup>-</sup>. The observed order of second-order rate constants for the S<sub>N</sub>2 reaction of unassociated X<sup>-</sup> with primary alkyl toluene-*p*-sulphonates is Cl<sup>-</sup>: Br<sup>-</sup>: I<sup>-</sup> = 8:3:1 (Me<sub>2</sub>SO; 25°),<sup>6</sup> 9:3:1 (HCONMe<sub>2</sub>; 0°),<sup>7</sup> 18:4:1 (Me<sub>2</sub>CO; 25°).<sup>5</sup> The much greater ratios observed in the molten R<sub>4</sub>N<sup>+</sup>X<sup>-</sup> show that this medium represents a further increase in dispersion of X<sup>-</sup> nucleophilicity, presumably both because there is some residual anion solvation (and deactivation) in dipolar aprotic solvents,<sup>8</sup> and because

TABLE

*Pyrolysis of (n-C<sub>6</sub>H<sub>11</sub>)<sub>4</sub>N/X<sup>1</sup>,X<sup>2</sup> mixtures at 180 ± 10°*

Reactants (mmol)		Products (mmol) <sup>a</sup>			Products (%)			Relative rate <sup>b</sup>		
X <sup>1</sup>	X <sup>2</sup>	n°(R <sub>4</sub> NX <sup>1</sup> )	n°(R <sub>4</sub> NX <sup>2</sup> )	n(RX <sup>2</sup> )	n(RX <sup>1</sup> )	n(R <sub>3</sub> N)	RX <sup>1</sup>	RX <sup>2</sup>	R <sub>3</sub> N	k(X <sup>2</sup> )/k(X <sup>1</sup> )
I <sup>-</sup>	—	0.101	—	0.096	—	0.100	95 <sup>c</sup>	—	100 <sup>c</sup>	—
Cl <sup>-</sup>	—	0.110	—	0.111	—	0.119	101 <sup>d</sup>	—	108 <sup>d</sup>	—
I <sup>-</sup>	Br <sup>-</sup>	0.105	0.102	0.0034	0.022	—	3.3	22	—	7.3
I <sup>-</sup>	Br <sup>-</sup>	1.005	0.101	0.068	0.044	—	6.8	44	—	8.1
Br <sup>-</sup>	Cl <sup>-</sup>	1.27	0.141	0.0243	0.109	—	1.9	77	—	76
Br <sup>-</sup>	Cl <sup>-</sup>	1.03	0.110	0.0027	0.025	—	0.26	23	—	85

<sup>a</sup> Trapped at -196° and determined by gas chromatography: all analyses in duplicate, precision ±2%. <sup>b</sup> Calculated from the expression  $k(X^2)/k(X^1) = \log\{n^\circ(R_4NX^2)/[n^\circ(R_4NX^2) - n(RX^2)]\} / \log\{n^\circ(R_4NX^1)/[n^\circ(R_4NX^1) - n(RX^1)]\}$ , which follows from the integrated first-order rate law. This assumes constant volume of the reacting melt; consequently we arranged the experiments to keep the decrease in volume during reaction [as judged from  $[n^\circ(R_4NX^1) - n(RX^1) + n^\circ(R_4NX^2) - n(RX^2)]/[n^\circ(R_4NX^1) + n^\circ(R_4NX^2)]$ ] less than ca 10%. <sup>c</sup> Trace of pent-1-ene detected. <sup>d</sup> No pent-1-ene detected.

the less reactive substrate, R<sub>4</sub>N<sup>+</sup>, causes a lower decrease in selectivity. We suggest that the fused-salt results provide the best model for the intrinsic relative nucleophilicities of the X<sup>-</sup> toward saturated carbon.

The ratios of substitution [equation (1)] to elimination [equation (2)]† products observed in mass-spectrometrically monitored pyrolyses of alkaloid methohalides were interpreted in terms of diminishing S<sub>N</sub>2 and increasing E2 reactivity in the order I<sup>-</sup>, Br<sup>-</sup>, Cl<sup>-</sup>, F<sup>-</sup>,<sup>9</sup> but the present results show that, instead, it is due to a greater increase in the E2 rate constants in the order I<sup>-</sup> < Br<sup>-</sup> < Cl<sup>-</sup> < F<sup>-</sup> than that for the S<sub>N</sub>2 rate constants. Comparison of the data for the strychnine methohalides at 330–360° with

those in the Table indicates the following relative E2 rates (temperature difference being ignored): Cl<sup>-</sup>:Br<sup>-</sup>:I<sup>-</sup> = 2400:15:1. These ratios are again much greater than those typical (e.g. 6:2:1 for X<sup>-</sup> dehydrobromination in acetone at 69.9°)<sup>10</sup> of dipolar aprotic solvents; they are perhaps more in line with the probably larger differences in basicity of X<sup>-</sup>.<sup>11</sup>

Acknowledgement is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

(Received, July 5th, 1971; Com. 1133.)

† Elimination competes with substitution in many of these alkaloid methohalide pyrolyses in contrast to our results; whether this is due to the structural difference in R<sub>4</sub>N<sup>+</sup>, the temperature difference (350–400° vs. 180°), or both, is not known.

<sup>1</sup> J. F. Bunnett, *Ann. Rev. Phys. Chem.*, 1963, **14**, 271.

<sup>2</sup> J. E. Gordon, in 'Techniques and Methods of Organic and Organometallic Chemistry', ed. D. B. Denney, vol. 1, Dekker, New York, 1969, ch. 3.

<sup>3</sup> J. E. Gordon, *J. Org. Chem.*, 1965, **30**, 2760.

<sup>4</sup> M. Hesse, W. Vetter, and H. Schmid, *Helv. Chim. Acta*, 1965, **48**, 674.

<sup>5</sup> S. Winstein, L. G. Savedoff, S. Smith, I. D. R. Stevens, and J. S. Gall, *Tetrahedron Letters*, 1960, No. 9, 24.

<sup>6</sup> R. Fuchs and K. Mahendran, *J. Org. Chem.*, 1971, **36**, 730.

<sup>7</sup> W. M. Weaver and J. D. Hutchison, *J. Amer. Chem. Soc.*, 1964, **86**, 261.

<sup>8</sup> A. J. Parker, *Chem. Rev.*, 1969, **69**, 1.

<sup>9</sup> M. Hesse and H. Schmid, *Annalen*, 1966, **696**, 85.

<sup>10</sup> D. Eck and J. F. Bunnett, *J. Amer. Chem. Soc.*, 1969, **91**, 3099.

<sup>11</sup> J. O. Edwards, *J. Amer. Chem. Soc.*, 1954, **76**, 1540; A. Allerhand and P. v. R. Schleyer, *ibid.*, 1963, **85**, 1233; I. M. Kolthoff, S. Bruckenstein, and M. K. Chantooni, jun., *ibid.*, 1961, **83**, 3927.