is shown in Fig. 4. The spectrum consists of over 60 hyperfine components with an average spacing of 0.1 to 0.2 gauss. The fact that there are not many more component lines giving rise to an unresolvable single broad line indicates that protons in similar positions on different rings may well have very similar splitting constants. The spectrum appears to be symmetrical about its center. The two most intense components are 2.83 ± 0.03 gauss apart and because of the similarity of their splitting to that of the corresponding lines in triphenylmethyl (2.77 ± 0.02 gauss),[6] this value was chosen as the splitting constant for all three para hydrogens. Calculations[5,13,14] indicate that spin densities decrease in approximately the same proportion at various ring positions in going from planar to propeller configurations of the radicals. If one assumes that the methyl group does not affect the spin densities at the other positions on the toluyl ring, one can, in the light of the discussion above and the similarity between the *para* coupling constant in triphenylmethyl and *o*-toluyldiphenylmethyl, take the *meta* and *ortho* splitting constants equal to those in triphenylmethyl, *i.e.* 1.1 ± 0.1 and 2.5 ± 0.1 gauss, respectively. Even with all these approximations of equivalence of protons on different rings one must assume, if one is to account for the relatively few lines observed, that the splitting due to the methyl protons is an integral multiple (or dividend) of one of the ring proton coupling constants.

Since the Q value for methyl protons has been found to be about equal to that for ring protons,[15] one would expect the methyl proton coupling constant to have approximately the same value as the coupling constant of the *ortho* proton of the substituted ring. The methyl proton coupling constant, therefore, should be about 2.5 gauss. Values of this constant below 1 gauss yielded calculated spectra in very poor agreement with the observed one. A series of calculations were carried out with the constant between 1 and 2.8 gauss. The best correspondence between theory and observation was at 2.2 ± 0.2 gauss; this calculated spectrum is exhibited in Fig. 4. Several discrepancies exist between the two spectra in Fig. 4, but the overall patterns are in reasonably good agreement.

These rather tentative assignments tend to indicate that the substituted methyl group does not alter the relative orientations of the rings very much, probably due to the fact that the rings are already twisted out of planarity in the unsubstituted triphenylmethyl. The results indicate that the spin density on the *ortho* carbon to which the methyl is attached is about 90% of the spin density on the other *ortho* carbons. Since both the electronic theory and the spectral analysis are subject to considerable uncertainty, this figure should not be taken too seriously.

Summary.—Chloride substitution in the *para* position increases slightly the spin density at the *ortho* carbon and rather more the spin density at the *meta* position. Methoxy substitution in the *para* position does not seem to affect the *meta* carbon spin density but increases considerably the spin density on the *ortho* carbon; the spin density on the oxygen appears to be small. C^{13} studies on these compounds are contemplated; these may throw light on the effect of substituents upon spin densities, a phenomenon that has not yet been well studied, and upon the question of the planarity of the methyl structure.[16]

NOTE ADDED IN PROOF.—It is interesting to compare the recent measurements[17] on tris-*p*-nitrophenylmethyl with those in the present study. In tris-*p*-nitrophenylmethyl the proton coupling constants are 1.14 ± 0.02 and 2.50 ± 0.02 gauss for the *meta* and *ortho* protons, respectively.

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(13) A. D. McLachlan, *J. Chem. Phys.*, **32**, 1488 (1960).

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(15) A. D. McLachlan, *Mol. Phys.*, **1**, 223 (1958); G. Vincow and G. K. Fraenkel, *J. Chem. Phys.*, **34**, 1333 (1961).

(16) M. Karplus and G. K. Fraenkel, *ibid.*, **35**, 1312 (1961).

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF NOTRE DAME, NOTRE DAME, INDIANA]

The Energy Dependence of Cross Sections of Some Ion–Molecule Reactions[1]

BY LOWELL P. THEARD AND WILLIAM H. HAMILL

RECEIVED OCTOBER 11, 1961

The energy dependence of reaction cross sections has been observed for various ion–molecule reactions. The secondary ions $C_4H_{10}Br_2^+$, $C_4H_9Br^+$, $C_4H_{10}Br^+$, $C_2H_6Br_2^+$ and $CHBr_2^+$ from C_2H_5Br; $C_6H_{14}I_2^+$ from *n*-C_3H_7I and $C_6H_{14}Cl^+$ from *s*-C_3H_7Cl indicate low energy limits of stability. Tropylium and substituted tropylium ions appear to result from reactions of CH_3^+, CD_3^+, $CHCl_2^+$ and CCl_3^+ with C_6H_6; they give evidence of transitions in reaction cross sections at *ca.* 1.3–2.0 ev. ion energy which are identified with instability resulting from head-on collisions.

Introduction

The recent literature on ion–molecule reactions reports comparatively few examples which are consistent with the point particle ion-induced dipole description.[2,3] It has been pointed out in recent publications[4,5] that for every ion–molecule interaction one must expect a transitional relative translational energy E_t above which only head-on encounters can occur. The functional dependence changes from $Q = f(E_e^{-1/2})$ for $E_e < E_t$ to $Q = f(E_e^{-1})$ for $E_e > E_t$, where E_e is the terminal ion energy, due to the repeller field, at the exit slit of the ionization chamber. At sufficiently high ion-molecule relative velocity the secondary ion

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(1) This article is based on a thesis submitted by L. P. Theard in partial fulfillment of the requirements for the Ph.D. Degree in the University of Notre Dame, June 1960. This work was performed under the auspices of the Radiation Laboratory, University of Notre Dame, supported in part by the U.S.A.E.C. under contract AT(11-1)-38.

(2) F. H. Field, J. L. Franklin and F. W. Lampe, *J. Am. Chem. Soc.*, **79**, 2419 (1957).

(3) G. Gioumousis and D. P. Stevenson, *J. Chem. Phys.*, **24**, 294 (1958).

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TABLE I

APPEARANCE POTENTIALS OF PRIMARY IONS FROM ETHYL BROMIDE

Ion	m/e	Abundance	Other prod.	Appearance potential, ev. This work	Lit.
$C_2H_5Br^+$	110	69.2		10.4 ± 0.2	10.7,[a] 10.49[b]
	108	71.5			10.56,[c] 10.29[d]
CH_2Br^+	95	4.9	CH_3	13.7 ± .2	14.1[a]
	93	6.6			
CHBr	94	1.2		15.0 ± .3	
	92	1.1		16.9 ± .5[e]	
CBr^+	93			19.8 ± .5	
	91	1.7		23.0 ± .4[e]	
				25.4 ± .4[e]	
HBr^+	82	4.0	C_2H_4	12.0 ± .2	
	80	4.1		17.0 ± .4[e]	
Br^+	81	15.2	C_2H_4 + H	16.5 ± .4	18.6[a]
	79	15.4			
C_2H_5	29	100	Br	11.2	11.4[a]
$C_2H_4{}^+$	28	21.0	HBr	12.3 ± .2	
$C_2H_3{}^+$	27	91.5	H_2 + Br	13.7 ± .2	
$C_2H_2{}^+$	26	32.5	H_2 + HBr	15.1 ± .4	
			2H + HBr	18.5 ± .5[e]	
			3H + Br	21.8 ± .6[e]	
$CH_3{}^+$	15	3.8	CH_2 + Br	15.8 ± .4	16.9[a]
				19.4 ± .4[e]	
$CH_2{}^+$	14	4.2		19.7 ± .4	

[a] Ref. 11. [b] J. D. Morrison and A. J. C. Nicholson, *J. Chem. Phys.*, **20**, 1021 (1952). [c] W. C. Price, *ibid.*, **3**, 365 (1935). [d] K. Watanabe, *ibid.*, **26**, 542 (1957). [e] Second and third values for a given ion refer to breaks in the ion abundance curves.

must become unstable and the linear Q *vs.* $E_e{}^{-1}$ plot passes through the origin. The present report and other recent work[5] describe additional examples of these effects.

The customary description of ion–molecule reactions in terms of ion-induced dipole forces should apply equally to ion-permanent dipole collisions if rotational freedom is not constrained at distances greater than those leading to capture for induced dipoles. The very large cross section reported for the reaction[6]

$$CH_3OH^+ + CH_3OH \longrightarrow CH_3OH_2{}^+ + CH_3O$$

indicated the need for further study of this reaction.

Experimental

The mass spectrometer and the method of measuring repeller field and electron energy dependence have been described.[4] The electron current was 10.5 microamp. and the ionizing voltage was 70 v. for all measurements.

Both primary and secondary ion currents, for variable repeller field, were measured with a vibrating reed electrometer (Applied Physics Corp., Model 30) and a Sargent multi-range recorder. Correction for pressure decay was applied for protracted measurements. Appearance potentials were measured by the method of vanishing current, with krypton or xenon for reference, using magnetic sweep and a repeller field of 12 v./cm.

Alkyl halides were reagent grade; methanol and ethanol were Fisher Certified Reagent grade; CD_3OH was obtained from Volk Radiochemical Co. All reagents were outgassed by vacuum trap-to-trap distillation.

Results

Reaction cross sections are determined, in the usual manner by

$$Q = i_s/i_pd_0N \qquad (1)$$

where d_0 = 0.127 cm. and N are ion path length and concentration of molecules. The ratio of secondary to primary ion currents, i_s/i_p must be corrected for depletion of primary ions by reaction only for reactions involving formation of CH_5O^+ etc. ions for methanol.

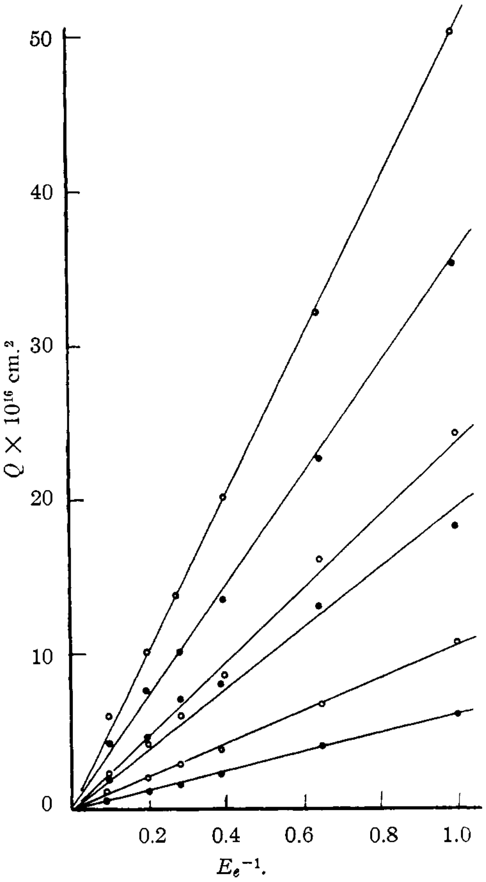

Fig. 1.—Dependence of reaction cross sections upon reciprocal ion energy in ev.$^{-1}$. From top-to-bottom the scaling factors of Q, secondary ions and reacting molecule are: 20, $C_4H_9Br^+$, C_2H_5Br; 5, $C_6H_{14}Cl^+$, *s*-C_3H_7Cl; 10, $C_6H_{14}I_2{}^+$, *n*-C_3H_7I; 5, $C_2H_6Br_2{}^+$, C_2H_5Br; 1, $C_4H_{10}Br^+$, C_2H_5Br; 10, $C_4H_{10}Br_2{}^+$, C_2H_5Br. Cross-sections for bromides and chlorides refer to the combined isotopic species.

Alkyl Halides.—Data for the primary and secondary ions from ethyl bromide appear in Tables I and II. The abundances of several secondary ions were too small for the measurement of appearance potentials. It should be noted that for four of these reactions there is a common activated complex $C_4H_{10}Br_2{}^+$ and that Q *vs.* $E_e{}^{-1}$ is linear for $E_e \gtrsim 1$ ev. with zero intercept (see Fig. 1). The ion $CHBr_2{}^+$ is not well characterized, either as to appearance potential or as to the energy dependence of Q.

No secondary ions appear in the high pressure spectrum of *n*-C_3H_7Cl, and two in that of *s*-C_3H_7Cl at m/e = 121 and 123 which correspond in intensity to $C_6H_{14}{}^{35}Cl^+$ and $C_6H_{14}{}^{37}Cl^+$. The appearance potentials of these ions (11.2 ev.) and of $C_3H_7{}^+$ (11.1 ev.) and $C_3H_7Cl^+$ (11.2 ev.) are substantially equal. The reaction is presumably

$$C_3H_7Cl^+ + s\text{-}C_3H_7Cl \longrightarrow C_6H_{14}Cl^+ + Cl \quad (A)$$

This was verified by the failure of $C_3H_7{}^+$ from added *i*-butane to enhance the yield of $C_6H_{14}Cl^+$.

Benzene Mixtures.—Appearance potentials are listed in Table III. The predominant cross-

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(6) D. O. Schissler and D. P. Stevenson, *J. Chem. Phys.*, **24**, 926 (1956).

TABLE II

SECONDARY IONS FROM ETHYL BROMIDE

Ion	Rel. abundance	Appearance potential, ev.	Reaction
$C_3H_2Br^+$	0.18		
$C_3H_4Br^+$	0.30		
$C_4H_9Br^+$	22.8	10.4 ± 0.2	$C_2H_5Br^+ + C_2H_5Br \longrightarrow C_4H_9Br^+ + HBr$
$C_4H_{10}Br^+$	100	10.6 ± .2	$C_2H_5Br^+ + C_2H_5Br \longrightarrow C_4H_{10}Br^+ + Br$
$CHBr_2^+$	4.1	14.0 ± .4	$CH_2Br^+ + C_2H_5Br \longrightarrow CHBr_2^+ + C_2H_6$
$CH_3Br_2^+$	0.57		
$C_2Br_2^+$	0.48		
$C_2H_6Br_2^+$	24.7	10.7 ± .2	$C_2H_5Br^+ + C_2H_5Br \longrightarrow C_2H_6Br_2^+ + C_2H_4$
$C_4H_{10}Br_2^+$	8.8	10.5 ± .2	$C_2H_5Br^+ + C_2H_5Br \longrightarrow C_4H_{10}Br_2^+$

TABLE III

MISCELLANEOUS APPEARANCE POTENTIALS

Primary	Secondary	Source	Appearance potential, ev.
s-$C_3H_7Cl^+$		s-C_3H_7Cl	11.0 ± 0.2
s-$C_3H_7^+$		s-C_3H_7Cl	11.1 ± .2
s-$C_3H_7^+$	$C_6H_{14}Cl^+$	s-C_3H_7Cl	11.2 ± .2
CD_3OH^+		CD_3OH	10.9 ± .2
CD_3OH^+	$CD_3OH_2^+$	CD_3OH	11.0 ± .2
CD_3OH^+	CD_3OHD^+	CD_3OH	10.9 ± .2
CCl_3^+		CCl_4	11.7 ± .2
CCl_2^+		CCl_4	15.9 ± .2
CCl_3^+	$C_7H_5Cl_2^+$	$CCl_4 + C_6H_6$	11.8 ± .2
$CHCl_3^+$		$CHCl_3$	11.5 ± .2
CCl_3^+		$CHCl_3$	12.9 ± .2
$CHCl_2^+$		$CHCl_3$	11.7 ± .4
CCl_2^+		$CHCl_3$	12.6 ± .4
$CHCl_2^+$	$C_7H_6Cl^+$	$CHCl_3 + C_6H_6$	11.7 ± .4
CH_3^+		CH_3I	12.3
CH_3^+	$C_7H_7^+$	$CH_3I + C_6H_6$	12.5 ± .2[a]
CD_3^+		CD_4	14.6 ± .2
CD_3^+	$C_7H_6D^+$	$CD_4 + C_6H_6$	14.4 ± .2
CD_3^+	$C_7H_5D_2^+$	$CD_4 + C_6H_6$	14.4 ± .2
CD_3^+	$C_7H_4D_3^+$	$CD_4 + C_6H_6$	14.4 ± .2
CD_3^+	$C_5H_5^+$	$CD_4 + C_6H_6$	14.8 ± .5
CD_3^+	$C_5H_4D^+$	$CD_4 + C_6H_6$	14.6 ± .5
CD_3^+	$C_5H_3D_2^+$	$CD_4 + C_6H_6$	14.8 ± .5
Xe^{*}[b]	CH_3Xe^+	$CH_3I + Xe$	11.7 ± .2
Xe^{*}	CH_3Xe^+	$CH_3Br + Xe$	11.7 ± .2
Xe^{*}	Xe_2^+	Xe	11.3 ± .4

[a] The heat of formation of $C_7H_7^+$ is 9.45 ev., according to A. G. Harrison, L. R. Honnen, H. J. Dauben, Jr., and F. P. Lossing, *J. Am. Chem. Soc.*, **82**, 5593 (1960). [b] An excited neutral species is the precursor.

TABLE IV

SECONDARY IONS FROM MIXTURES CONTAINING BENZENE[a]

Ion	Rel. abundance	Ion	Rel. abundance
($CH_3I + C_6H_6$)		($CHCl_3 + C_6H_6$)	
$C_7H_6^+$	15.9		
$C_7H_7^+$	100	$C_7H_5^+$	13.7[b]
$C_7H_8^+$	5.7	$C_7H_6^+$	3.2[b]
C_3HI^+	3.5	$C_7H_7^+$	13.9[b]
$C_3H_2I^+$	2.8	$C_5H_4Cl^+$	10.3
C_4HI^+	2.0	$C_7H_6Cl^+$	100
$C_4H_4I^+$	0.3	$C_5H_3Cl_2^+$	3.5
C_5HI^+	0.5	$C_7H_5Cl_2^+$	2.3
C_6HI^+	2.1		
$C_6H_5I^+$	3.3	($CD_4 + C_6H_6$)	
$C_7H_6I^+$	0.4		
		$C_7H_6D^+$	21.5
($CCl_4 + C_6H_6$)		$C_7H_5D_2^+$	100
		$C_7H_4D_3^+$	28.7
$C_7H_5^+$	52.0[b]		
$C_7H_6^+$	19.5[b]	($CD_4 + C_6H_6$)	
$C_5H_4Cl^+$	36.2		
C_6HCl^+	6.8	$C_5H_4D^+$	100
$C_7H_6Cl^+$	92.6	$C_5H_3D_2^+$	49.2
$C_7H_5Cl_2^+$	100	$C_5H_2D_3^+$	19.1
$C_5H_2Cl_3^+$	4.2		
$C_7H_4Cl_3^+$	0.7		

[a] Reservoir pressure 400 microns of each component; electron energy 70 v., repeller field 2.8 v. cm.$^{-1}$. [b] Enhanced yields of ions which appear in the high pressure spectrum of benzene.

product in benzene–methyl iodide mixtures is $C_7H_7^+$ (there are ten others, see Table IV), which is also a minor product of the high pressure reactions of benzene alone. We find, for the mixture, an appearance potential $A(C_7H_7^+)$ = 12.5 ev. which corresponds to $A(CH_3^+)$ = 12.3 ev. from methyl iodide. The reported appearance potentials of all primary ions from benzene differ from $A(C_7H_7^+)$ by at least 2 ev. and those from methyl iodide, excepting CH_3^+, by at least 0.7 ev.[7-9] The reaction appears to be

$$CH_3^+ + C_6H_6 \longrightarrow C_7H_7^+ + H_2;\ \Delta H = -2.8 \text{ ev.} \quad \text{(B)}$$

since the alternative reaction giving 2H would be 1.7 ev. endothermic, based on $\Delta H_f(C_7H_7^+)$ = 9.45 ev. This assignment is supported by the appearance potentials in Table III for various D-substituted ions related to $C_7H_7^+$ and $C_5H_5^+$. The appearance potential of $C_5H_2D_3^+$ could not be established because of interference by the pressure-broadened base of a primary peak.

The high pressure spectra of carbon tetrachloride and of chloroform contain no evidence of secondary ions. There is no detectable CCl_4^+ and negligible $CHCl_3^+$. The halogen-containing secondary ions of greatest interest evidently form by reactions

$$CCl_3^+ + C_6H_6 \longrightarrow C_7H_5Cl_2^+ + HCl \quad \text{(C)}$$

and

$$CHCl_2^+ + C_6H_6 \longrightarrow C_7H_6Cl^+ + HCl \quad \text{(D)}$$

or the like. There is evidence of a coherent pattern of reactions among the various methyl- and substituted methyl-ions which is most clearly demonstrated by the reactions involving CD_3^+.

The cross sections for reactions B, C, D as functions of ion energy appear in Fig. 2.

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(7) A. Hustrulid, P. Kusch and J. T. Tate, *Phys. Rev.*, **54**, 1037 (1938).

(8) H. Bronson and C. Smith, *J. Am. Chem. Soc.*, **75**, 4133 (1953).

(9) R. F. Pottie, R. Barker and W. H. Hamill, *Radiation Research*, **10**, 644 (1959).

Reactions with Noble Gases.—The following reactions were indicated

$$Xe^* + CH_3I \longrightarrow CH_3Xe^+ + I^- (?) \qquad (E)$$

$$Xe^* + CH_3Br \longrightarrow CH_3Xe^+ + Br^- (?) \qquad (F)$$

$$Xe^+ + CH_3I \longrightarrow CH_3Xe^+ + I \qquad (G)$$

$$Xe^+ + CH_3Br \longrightarrow CH_3Xe^+ + Br \qquad (H)$$

There is no direct evidence for anion formation. For reactions E and F, the appearance potential $A(CH_3Xe^+)$ is 11.7 ± 0.2 ev. compared to 12.13 for Xe^+. At higher electron energy the reactions G and H must predominate since the cross sections diminished strongly with increasing repeller field whereas reactions between neutral species are only slightly affected. Other results, for which the reactive primary species could not be established, appear in Table V.

TABLE V

SECONDARY IONS CONTAINING NOBLE GAS ATOMS

Ion	Reaction mixture contains	Ion	Reaction mixture contains
CH_3Xe^+	CH_3Cl	$XeBr^+$	C_2H_5Br
CD_3Xe^+	CD_4	XeI^+	CH_3I
CH_3Kr^+	CH_4	$KrBr^+$	C_2H_5Br
CKr^+	CH_4	XeO^+	O_2
$XeCl^+$	CH_3Cl	KrO^+	O_2

Persistent Collision Complexes.—Collision complexes of the type

$$M^+ + M \longrightarrow M_2^+$$

have previously been reported for ethyl iodide, ethyl bromide, *n*-propyl iodide and the mixed methyl iodide–ethyl iodide.[10] The only additional reaction found in the present work is

$$n\text{-}C_3H_7Br^+ + n\text{-}C_3H_7Br \longrightarrow C_6H_{14}Br_2^+$$

Negative results were obtained at *ca.* 400 micron reservoir pressure for the mixtures: n-C_3H_7I + C_2H_5Br; n-C_3H_7I + C_2H_5Cl; C_2H_5Br + C_6H_5Br; C_2H_5Br + C_2H_5Cl; C_2H_5Br + n-C_4H_{10}; C_2H_5Br + C_2H_6; C_2H_5Br + cyclo-C_6H_{12}; Xe + H_2O; Ar + H_2O; Xe + C_3H_7I; Xe + C_2H_5Br; Kr + C_2H_5Br.

Methanol.—Appearance potential measurements for methanol-d_3 appear in Table III, and the cross sections of the protonated secondary ions by self reactions in Table VI. The two secondary ions arising from CD_3OH^+ and CD_3OH at a common appearance potential are plausibly, but arbitrarily, shown as $CD_3OH_2^+$ and CD_3OHD^+.

TABLE VI

CROSS SECTIONS FOR METHANOL

		Grad. v. cm.$^{-1}$			
		12	28	40	80
Primary	Secondary	Cross section × 10^{16} cm.^{2}			
CD_3OH^+	$CD_3OH_2^+$	232	127	90	57
CD_3OH^+	CD_3OHD^+	176	98	73	44
CH_3OH^+	$CH_3OH_2^+$	445	244	198	102

Discussion

The reaction producing CH_2Br^+ (Table I) differs from that chosen by Irsa,[11] *viz.*

$$C_2H_5Br + e \longrightarrow CH_2Br^+ + CH + H_2 + 2e \qquad (K)$$

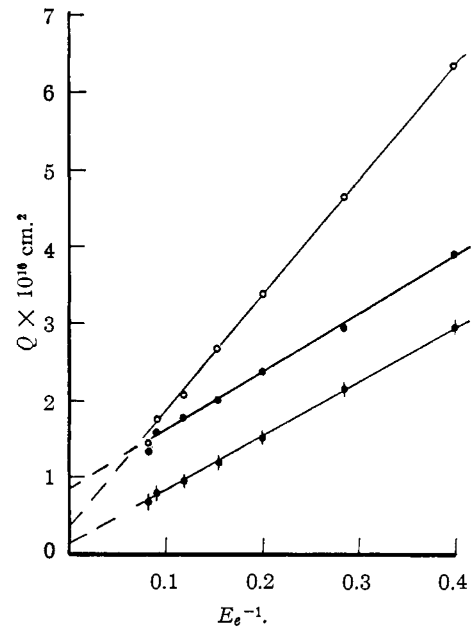

Fig. 2.—Dependence of reaction cross sections upon reciprocal ion energy in ev. From top-to-bottom the scaling factors of Q, secondary ion and reactants are: 0.1, $C_7H_7^+$, CH_3^+ + C_6H_6; 1, $C_7H_6Cl_2^+$, CCl_3^+ + C_6H_6; 0.1, $C_7H_6Cl^+$, $CHCl_2^+$ + C_6H_6. Cross sections for chlorides refer to combined isotopic species.

for which the calculated ΔH = 14.9 ev. Taking 171 kcal./mole for the heat of sublimation of carbon[12] and the ionization potential[13] $I(CH_2Br)$ = 9.30 ev., we obtain ΔH = 17.7 ev. for reaction K.

From the present measurement at high pressure of chloroform we find $A(CCl_3^+)$ = 12.9 ± 0.2 ev. Combining this value with $I(CCl_3)$ = 8.78 ± 0.05 ev.[14] gives $D(CCl_3\text{–}H)$ = 95 ± 6 kcal./mole. Farmer, *et al.*,[14] had obtained 88.9 ± 3 kcal./mole based upon $A(CCl_3^+)$ from CCl_4 and CCl_3Br.

The value $A(C_3H_7^+)$ = 11.1 ± 0.2 ev. from s-C_3H_7Cl combines with $I(s\text{-}C_3H_7)$ from the work of Lossing and DeSousa[15] to give $D(s\text{-}C_3H_7\text{-}Cl)$ = 74 kcal./mole.

The dependence of Q upon ion energy E has usually been considered to be linear in $E^{-1/2}$. None of the present results conforms to this description. We have found that the development of Gioumousis and Stevenson,[3] valid for point particles and ion-induced dipole forces, should be modified to allow for short range repulsive forces.[4,5] That is

$$Q = P_L E_e^{-1} \int_0^{E_e} (\sigma_L E^{-1/2} - \sigma_K) \mathrm{d}E + P_K E_e^{-1} \int_0^{E_e} \sigma_K \, \mathrm{d}E \qquad (2)$$

$$= 2 P_L \sigma_L E_e^{-1/2} + (P_K - P_L)\sigma_K \qquad (3)$$

where $$\sigma_L = \pi e(\alpha(m_1 + m_2)/m_2)^{1/2} \qquad (4)$$

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(10) R. F. Pottie and W. H. Hamill, *J. Phys. Chem.*, **63**, 877 (1959).

(11) A. P. Irsa, *J. Chem. Phys.*, **26**, 18 (1957).

(12) J. D. Morrison and H. E. Stanton, *ibid.*, **28**, 9 (1958).

(13) F. P. Lossing, P. Kebarle and J. B. DeSousa "Advances in Mass Spectrometry," Pergamon Press, New York, N. Y., 1959, pp. 431–442.

(14) J. B. Farmer, I. H. S. Henderson, F. P. Lossing and D. G. H. Marsden, *J. Chem. Phys.*, **24**, 348 (1956).

(15) F. P. Lossing and J. B. De Sousa, *J. Am. Chem. Soc.*, **81**, 281 (1959).

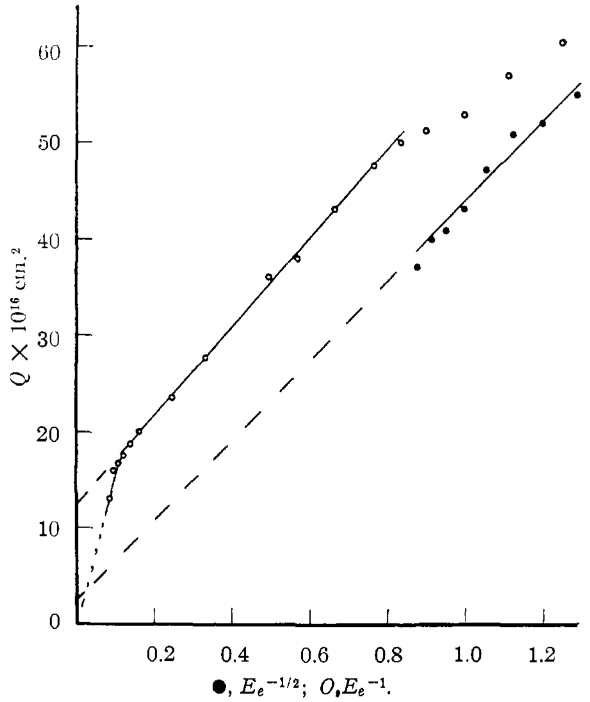

Fig. 3.—Dependence of reaction cross section upon ion energy for the combined products $C_7H_4D_3^+$, $C_7H_5D_2^+$, $C_7H_6D^+$ from CD_3^+ and C_6H_6. Ordinates for the lower curve have been shifted down by 10^{-15} cm.^{2}.

and α, m_1 and m_2 are the molecular polarizability and the masses of ion and molecule, respectively. σ_K corresponds to a gas kinetic cross section for head-on collisions, considered to be independent of energy, and the P's are reaction probabilities, also taken to be independent of energy over limited ranges. It is evident that equation 2 can be valid only for $0 < E < E_t$ where

$$E_t = (\sigma_K/\sigma_L)^2 \qquad (5)$$

For $E_e > E_t$ it follows that equation 3 applies for $0 < E < E_t$ over the first part of the ion trajectory and equation 6 applies over the subsequent region for which $E_t < E < E_e$

$$Q = (P_L\sigma_L E_t^{1/2})E_e^{-1} + P_K\sigma_K \qquad (6)$$

If the secondary ion decomposes rapidly after formation after an encounter at E_c and if $E_c < E_t$, then

$$Q = (2P_L\sigma_L E_c^{1/2} + (P_K - P_L)\sigma_K E_c)E_e^{-1} \qquad (7)$$

If $E_c > E_t$, then equations 3 and 6 apply in the low energy ranges and equation 7 in the high range. Unless P_K in equation 6 is zero, and this possibility certainly cannot be excluded, the transition E_c will be exhibited by a change in slope of Q *vs.* E_e^{-1}.

For the secondary ions arising from alkyl halides, excepting $CHBr_2^+$, Q is linear in E_e^{-1} from 1 to 10 ev. and the intercept is substantially zero (see Fig. 1). Measurements at lower ion energy were considered to be unreliable so that the applicability of equation 3 could not be tested. In the context of other work[5,16] we interpret these results in terms of equation 6, with $P_K \cong 0$, since this condition frequently holds, but we cannot exclude the applicability of equation 7. In the latter case, by considering the combined yields of the 4 secondary ions arising from the common complex $C_4H_{10}Br_2^+$, we find that if $\Sigma P_L \cong 1$, then $E_c \cong 0.02$ ev. Contrariwise it would follow that $\Sigma P_L << 1$.

The data of Tables III and IV for reactions involving C_6H_6 and CX_3^+ (where X = H, D or Cl) suggest the $C_7H_{7-n}X_n^+$ ions are tropylium and D- or Cl- substituted tropylium ions.[17] We have not been able to devise a mechanism to account for the relative yields of isotopically mixed products, either in $C_7H_{7-n}D_n^+$ or in $C_5H_{5-m}D_m^+$ ions. Since their appearance potentials are indistinguishable, it may be that C_7-ion → C_5-ion. The decomposition of primary $C_7H_7^+$ gives rise to a metastable peak m/e = 46.4.[17] The possibility of observing the secondary spectrum metastable peak at m/e = 46.4 is excluded by a relatively very large ion current at m/e = 48.[18]

The linear dependence of Q upon E_e^{-1} for the C_7-ions is demonstrated in Fig. 2. Other measurements at lower repeller fields and customary accelerating voltages do not conform to the behavior shown, nor to the Q *vs.* $E_e^{-1/2}$ linear dependence because of instrumental characteristics. It has since been found[16] that secondary ion behavior at low repeller fields can be successfully observed at reduced accelerating voltages. The $C_7H_6D^+$ secondary ion from benzene–methane-d_4 has recently been re-examined[18] at 462 v. accelerating voltage and the results appear in Fig. 3. Both $Q - E_e^{-1}$ and $Q - E_e^{-1/2}$ linear dependences appear as well as indications of a break at $E_e \cong 8$ ev. which is also suggested in Fig. 2. The values of Q in Fig. 3 are 7.0 times the values actually observed for $C_7H_6D^+$ in order to approximate the combined yields of all three C_7-ions arising from the common complex $C_7H_6D_3^+$.

The secondary tropylium-type ion of largest cross section is $C_7H_7^+$, for which the measured slope from Fig. 2 is 120 × 10^{-16} cm.^{2} ev.$^{-1}$ If equation 6 applies and P_L = 1, the calculated slope is 82 × 10^{-16} cm.^{2} ev.$^{-1}$ Similarly for $C_7H_6Cl^+$ the observed slope is 58 × 10^{-16} cm.^{2} ev. (or 20% greater if $C_7H_7^+$ and $C_7H_5Cl_2^+$ from the same complex are included), and the calculated value is 102 × 10^{-16} cm.^{2} ev.$^{-1}$ if P_L = 1. In each instance the measured slope would be about 10% larger if C_5-ions were included.

Referring to equations 3–7 and Fig. 3 we find $P_L\sigma_L = 12 \times 10^{-16}$ cm.^{2} from the lower curve. Taking $E_t^{1/2}$ observed as 1.3 ev., the upper curve gives $P_L\sigma_L \cong 35 \times 10^{-16}$ cm.^{2} The calculated value of σ_L is 58 × 10^{-16} cm.^{2}

Persistent collision complexes have been observed only between alkyl bromides or between alkyl iodides, except for $N_2^+ + N_2 \rightarrow N_4^+$ which occurs with very small cross section.[19] Although the alkyl groups may differ for reactions involving alkyl halides, the halogen may not. These facts suggest a three-electron bonded structure, RX⁝XR$^+$. This is consistent with the interpretation

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(17) P. N. Rylander, S. Meyerson and H. M. Grubb, *J. Am. Chem. Soc.*, **79**, 842 (1957).

(18) We are indebted to Mr. G. F. Hennion, Jr., for these measurements.

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that the vacancy in RX^+ arises from a non-bonding electron with RI or RBr but from a bonding electron with RCl.[20] Also, there may be substantial resonance for $R'\,X{:}X\,R''^+$, *viz.* similar X and dissimilar R, but in general rather less for $R\,X'{:}\,X''\,R^+$. It has been estimated that the bond dissociation energies are $D(RBr{:}BrR^+) = 20$ kcal./mole and $D(RI : IR^+) \cong 16$ kcal./mole.[21]

Rare gas–water mixtures were examined because of the well known hydration of gaseous ions observed in ion mobility measurements.[22] The present results suggest that XeH_2O^+ formation would require a triple collision.

When the experiments with methanol were performed, it was intended to investigate the possibility of locked-in ion-permanent dipole interaction since the cross sections are much too large to be accounted for in terms of a freely rotating dipole.[21] We have recently learned that the CHO^+ and CH_3O^+ ions also contribute importantly to $CH_3OH_2^+$ formation.[23] The appearance potentials in Table III can only demonstrate the involvement of the ion of lowest appearance potential,[24] CH_3OH^+. Consequently it is impossible to analyze the data of Table VI. If the Q *vs.* $E_e^{-1/2}$ dependence applied to each contributing reaction, it would also describe their linear combination. In fact, it does not. If the ion-permanent dipole force law applies, *i.e.*

$$V = -e\mu r^{-2}\cos\theta$$

there are two limiting cases. If the dipole is rotating freely, the contribution to reaction cross section is averaged out and there remains the ion-induced dipole contribution. If the dipole "locks in" on the ion with $\theta = 0°$, then

$$QE_e = \sigma \ln (E_e/E_i)$$

where σ represents collected constants and E_i is the initial (thermal) ion energy. The applicability of this equation cannot be tested adequately, but qualitatively it can account for the very large measured cross section obtained from equation 1.

Acknowledgment.—We are indebted to Professor J. L. Magee and Dr. John V. Dugan, Jr., for helpful discussions.

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[24] Most of the published reaction cross sections are unreliable because of possible involvement of primary ions other then the one reported, *viz.* that reacting primary ion of lowest appearance potential. When only one primary ion is involved, the calculated cross section will be constant over a range of ionizing voltage.

[CONTRIBUTION FROM THE CHEMISTRY DIVISION, RESEARCH DEPARTMENT, U. S. NAVAL ORDNANCE TEST STATION, CHINA LAKE, CALIFORNIA]

Halide Complexes of Cobalt(II) in Acetone Solution[1]

BY DWIGHT A. FINE

RECEIVED AUGUST 17, 1961

Chloride, bromide and iodide complexes of cobalt(II) in acetone solution have been studied spectrophotometrically. Complexes having 2, 3 and 4 coördinated halides have been detected, and the absorption spectra of the individual complexes have been determined. The spectra of the dihalo and trihalo complexes were determined by the mole ratio method; the spectra obtained in concentrated halide solutions are identical with the known spectra of the tetrahalo complexes. Approximate values of equilibrium constants for the different species have been obtained. The absorption spectra indicate that all of the species are tetrahedral in structure.

Introduction

Previous investigations of cobalt(II) halide systems in organic solvents have indicated the possible presence of complexes having from one to four coördinated halides.[2-5] Characterization of the individual complexes is of interest; knowledge of the nature of these species and of their absorption spectra would be an aid in interpreting spectral measurements of aqueous solutions, solid media and ionic melts. The spectra would also be of interest to ligand field theory.

Katzin and Gebert[4] made an extensive study of cobaltous chloride in organic solvents, using the method of continuous variations. Their results indicated the presence of species having chloride to cobalt ratios of 2, 3, and 4. The peaks observed in the spectra of the solutions were assigned to the different species, but the complete spectra of the individual species were not elucidated. The subsequent development of more powerful experimental tools and methods, and of the ligand field theory, has made a more rapid and conclusive investigation possible. The present investigation makes use of the Cary recording spectrophotometer, and the mole ratio method for the determination of complexes. The investigation was confined to a single solvent, acetone.

Experimental

Apparatus.—All absorption spectra were measured on a Cary Recording Spectrophotometer Model 14, Serial 244. Matched quartz cells of 1 cm. or 5 cm. path length were employed. It was not possible to maintain constant ionic strength in acetone solution; concentrations were therefore kept as dilute as possible in order to minimize changes in activity coefficients and also to minimize danger of deviation from Beer's Law. The use of the 5 cm. cells was found convenient for this purpose.

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