These values are smaller than those found for the dissociation of the contact $\sim S^-,Na^+$ ion pairs in the above solvents, namely, −60 and −63 eu, and larger than those characterizing the dissociation of the solvent-separated Na^+,BPh_4^- ion pairs, *i.e.*, 23 and 24 eu, respectively. This may indicate a lower degree of coordination of the free Cs^+ ion than that of Na^+ ion, a very plausible conclusion. However, one would expect $-\Delta S$ for $\sim S^-,Cs^+$ dissociation to be substantially larger in DME than in THF, and this is hardly the case. A similar situation is found for the dissociation of Cs^+,BPh_4^- ion pairs in these two solvents,[6] the respective $-\Delta S$ values being 32 and 33 eu. The dissociation constant of both cesium salts is about 20-fold smaller in THF than in DME (at 25°), but this change arises only from a decrease in the respective ΔH_{Diss}, ΔS_{Diss} being virtually constant. It is possible that the concept of two thermodynamically distinct ion pairs does not apply to these systems.[11,12]

Acknowledgment. The financial support of this investigation by the National Science Foundation and by the Petroleum Research Fund administered by the American Chemical Society is gratefully acknowledged.

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[11] M. Szwarc, *Makromol. Chem.*, **89**, 44 (1965).

[12] P. Chang, R. V. Slates, and M. Szwarc, *J. Phys. Chem.*, **70**, 3180 (1966).

Spectroscopic Evidence for Ionic Processes of γ-Irradiated Alkyl Iodides at −196°[1]

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Contribution from the Department of Chemistry and Radiation Laboratory,[3]
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Abstract: The optical absorption bands produced by γ irradiation of alkyl iodides in alkane matrices at −196° can be assigned to three species: 370 and 440 mμ, A; 390 and 480 mμ, B; 540 and 760 mμ, C. All are suppressed by positive charge traps, only B by electron traps. Isothermal relaxation in a soft matrix shows that A → B, A → C, and C → B. Only A appears initially at small RI, but all appear at large RI. Assignments are $A = RI^+$, $B = RI \cdot I$, $C = (RI)_2^+$. The ^2P states of RI^+ account for the separations of the A bands. Efficient formation of $RI \cdot I$ is attributed to ion recombination between RI^+ and I^-. The optically excited complex, RI^+I^-, has doublet character attributable to mixing of the ^2P states of RI^+, accounting for the B bands. Moreover, the known toluene and mesitylene (Ar) charge-transfer complexes with I were shown to form predictably from combination of Ar^+ with I^-. The assignment of C bands is supported semiquantitatively by previously reported excited states of persistent collision complexes of RI^+ and RI from mass spectrometry. These processes account for the major radiolytic effects. The formation of an identifiable charge-transfer complex $A \cdot C$ by recombination of C^+ and A^- provides the possibility, in suitable instances, of resolving a major mechanistic problem in radiation chemistry.

Repeated comparative studies of the photolysis and radiolysis of liquid alkyl iodides have shown limited similarities.[4] These are likely to arise principally from the weak C–I bond and geminate radical–atom interactions rather than from similarities of primary processes. A much better correlation was found between the results from radiolysis and ion–molecule reactions[5,6] but this may prove to be only a *tour de force*. Dissociative electron attachment of alkyl chlorides, bromides, and iodides in a hydrocarbon matrix at −196[7a] is consistent with their radiation chemistry at ~20°,[4,6] and similar studies support the interpretation that it can be a major radiolytic mechanism.[7b] The fates of the positive ions in liquid and solid alkyl iodides have not been determined, but recent work with γ-irradiated alkyl iodides in rigid matrices at −196° shows fairly complicated optical absorption spectra. These are due in part to positive ions and vary with concentration, with optical excitation, and with matrix relaxation.[8,9]

In a matrix of 3-methylpentane (3MP) both the electron and the (positive) hole migrate and are trapped by methyl iodide.[8] The sign of electric charge associated with a given species of color center, or with its precursor, can be inferred by the effect of tested additives. Thus, an additive known to trap holes depresses yields of positively charged color centers, and also enhances yields of anionic color centers by interfering with their destruction through charge recombination. Electron trapping additives operate analogously. Thus, the band at ~390 mμ from I_2, HI, CH_3I, and p-$C_6H_4I_2$ in 3MP following γ irradiation was depressed by CH_3Cl and attributed to I^-.[8] The 390-mμ band has since

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[1] This article is based upon a dissertation submitted by J. P. Mittal in partial fulfillment of the requirements for the Ph.D. degree at the University of Notre Dame.

[2] Peter C. Reilly Fellow; on leave of absence from Bhabha Atomic Research Center, Trombay, Bombay, India.

[3] The Radiation Laboratory of the University of Notre Dame is operated under contract with the U. S. Atomic Energy Commission. This is AEC Document No. COO-38-536.

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[5] R. F. Pottie, R. Barker, and W. H. Hamill, *Radiation Res.*, **10**, 644 (1959).

[6] H. A. Gillis, R. R. Williams, and W. H. Hamill, *J. Am. Chem. Soc.*, **83**, 17 (1961).

[7] (a) D. W. Skelly, R. G. Hayes, and W. H. Hamill *J. Chem. Phys.*, **43** 2795 (1965); (b) J. B. Gallivan and W. H. Hamill, *Trans. Faraday Soc.*, **61**, 1960 (1965); J. A. Ward and W. H. Hamill, *J. Am. Chem. Soc.*, **87**, 1853 (1965).

[8] E. P. Bertin and W. H. Hamill, *ibid.*, **86**, 1301 (1964).

[9] (a) R. F. C. Claridge and J. E. Willard, *ibid.*, **89**, 510 (1967); (b) *ibid.*, **88**, 2404 (1966).

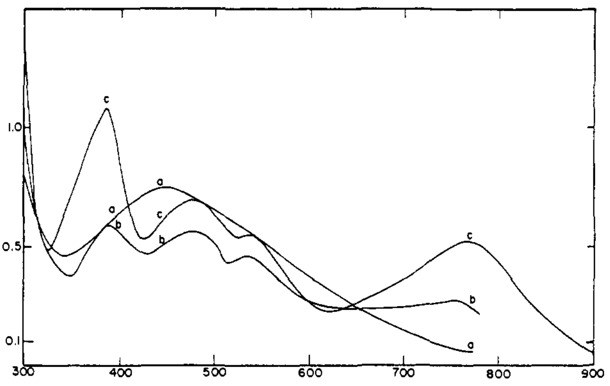

Figure 1. (a) Methyl iodide (0.05%) in 3-methylpentane immediately after irradiation; dose: 1.55×10^{19} ev/g; (b) same sample as preceding after 75-sec bleaching, tungsten light; (c) methyl iodide (0.05%) in 50:50 3MP–IP immediately after irradiation.

been shown to increase with time, requiring a new assignment.[9] All other bands of CH_3I have positive character.[8] Further study of these color centers has been undertaken to improve our understanding of ionic processes in general and of alkyl halides in particular.

Experimental Section

Phillips pure grade 3-methylpentane was passed successively through two 6-ft columns of Fisher 28–200 mesh silica gel and the middle fraction was retained each time. Gas chromatographic analyses indicated that unsaturates were reduced below 10^{-3} *M*. The major impurity was 2-methylpentane, which is not objectionable. Phillips pure grade isopentane (IP) was purified similarly. Solvents purified by this technique did not absorb above 220 mμ. Phillips research grade 2-methylpentene-1 (2MP-1) was passed through a 3-ft column packed with basic alumina (Woelm). The drying and purification of 2-methyltetrahydrofuran (MTHF) was carried out by passing it through a 3-ft column of alumina. Phillips pure grade toluene was passed through a 3-ft column of alumina. Mesitylene, Aldrich Puriss grade, was used as received. Fisher certified reagent grade methyl iodide was used as received.

Samples of 5 ml were prepared volumetrically in 1 × 1 cm Suprasil cells, without deaeration, and immersed in liquid nitrogen. They were irradiated and examined using a Cary Model 14R spectrophotometer. The IR-2 (tungsten) lamp of the spectrophotometer served for optical bleaching. The Corning filter 3385 transmits wavelengths longer than 520 mμ. The dose rate, using a 4-kcurie source and Fricke dosimetry, was 1.5×10^{18} ev ml^{-1} min^{-1} and all irradiations lasted 5 min unless otherwise stated.

Results

Complicated changes in the spectrum of irradiated CH_3I in 3MP at −196° with changing concentration have been attributed to pairing, or clustering, of permanent dipoles in the low dielectric medium.[8] When these trap positive charge, there is the possibility of ion–molecule reactions to form a variety of ionic species.[5] In sufficiently dilute solutions of CH_3I the spectrum was actually much simpler, consisting apparently of a single very wide band beginning at −775 mμ (Figure 1, spectrum a). After 75-sec optical bleaching the band maximum at 440 mμ has been suppressed with formation (or disclosure) of bands having maxima at 395, 480, 540, and 760 mμ (Figure 1, spectrum b).[10] In a softer matrix of 50:50 3MP–IP[11] the same four bands appear simply by isothermal relaxation, but the 390-mμ band is now relatively much larger (Figure 1, spectrum c).[11] At ~1% CH_3I in 3MP, all four of these bands appear immediately after irradiation.[8,9]

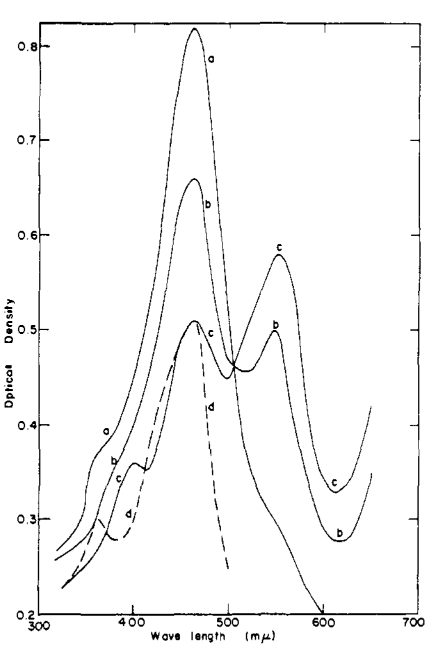

Figure 2. (a) 1-Iodopentane (1%) in 3MP immediately after irradiation; dose: 6.20×10^{18} ev/g; (b) same sample after 75-sec bleaching with Corning No. 3385 filter ($\lambda > 550$ mμ); (c) same sample after additional 75-sec bleach; (d) difference of spectra a and c.

The higher alkyl iodides differ from CH_3I qualitatively only in having an additional weak band at ~360 mμ.[9b] This is shown for 1-iodopentane in Figure 2, spectrum a, together with the much stronger 440-mμ band. Bleaching for 1.2 (c) and 2.5 min (d) removed the 360- and 440-mμ bands, shown by the difference spectrum d, while the 540- and 760-mμ bands (the latter not shown in Figure 2) increased strongly, with a small 390-mμ band also appearing. In an otherwise similar run with a sample also containing 5% MTHF, *none* of the RI bands could be detected. In comparable experiments with 0.05% CH_3I in 3MP, either 2% MTHF or 2% 2MP-1 suppressed all bands for $\lambda \gtrsim 300$ mμ. There is no absorption attributable either to positive or negative ions deriving from RI when holes are effectively trapped by a second additive and electrons are trapped by RI alone.

The 540- and 760-mμ bands probably arise from a single species, although the complexity of the spectrum may somewhat obscure this assumed relationship. For 1% C_2H_5I in 3MP it should first be noted that the 540- and 760-mμ bands are initially strong compared to the 440-mμ band (Figure 3). Also, that their ratio is nearly constant during isothermal relaxation. Substantially the same growth of 540- and 760-mμ bands from the 440-mμ band was observed for 1% CH_3I in 3MP by progressive bleaching, and the 390-mμ band was also well defined (*cf.* ref 8, Figure 8). It is quite impossible to conclude, however, whether decay of 440-mμ absorption increases 390-mμ absorption, or merely uncovers it.[8] The 390-mμ band is also resistant

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(10) Band maxima are practically the same for several alkyl iodides and shift somewhat with RI per cent and history. For identification purposes, however, it will be convenient to use a single representative λ_{max} to designate each band. We adopt the values 360, 390, 440, 480, 540, and 760 mμ.

(11) The viscosities in poise at −196° for 3MP–IP mixtures, in volume % 3MP, are: 100%, 9.4×10^{11}; 70%, 1.4×10^{10}; 50%, 5.9×10^{8}; 20%, 1.8×10^{7}; data from J. P. Lombardi, J. W. Raymonda, and A. C. Albrecht, *J. Chem. Phys.*, **40**, 1148 (1964).

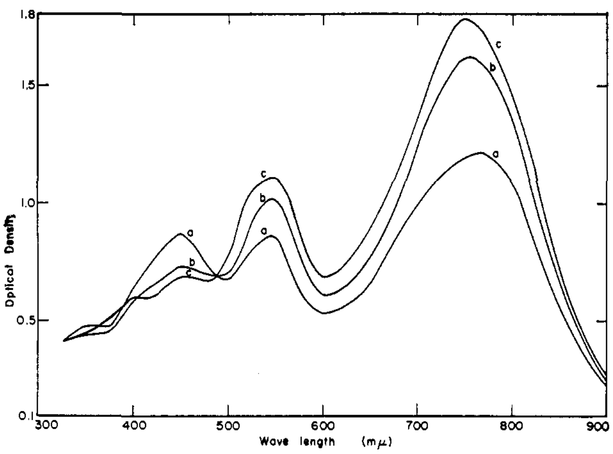

Figure 3. Ethyl iodide (1%) in 3-methylpentane at 77°K; dose 7.75 × 10^{18} ev/g: (a) immediately after irradiation; (b) same sample after 1 hr of dark decay; (c) same sample after 2 hr of total dark decay.

to optical bleaching. The relationship of the color centers responsible for 390- and 440-mμ absorption was finally established using 0.05% CH_3I in 70:30 3MP–IP and isothermal relaxation. The spectrum (Figure 4a) is almost pure 440-mμ absorption initially, with a marked growth of 390-mμ absorption after 1 (b) and 2 hr (c). There was also 540- and 760-mμ-band growth. The latter are optically bleached (d), the slight decrease in 390-mμ absorption being entirely attributable to decrease in the underlying absorption at $\lambda \geq 440$ mμ. A notable feature of the spectra in Figure 4 is the well-resolved band at 480 mμ which appears to be associated with the strong 390-mμ band. The same correlation appears for n-C_4H_9I (spectra 4 and 5, Figure 4 of ref 9b). The 480-mμ band can only be detected clearly when 440- and 540-mμ absorptions are removed by thermal relaxation or optical bleaching and, like the 390-mμ band, apparently derives from 540- and 760-mμ isothermal decay but not from optical bleaching. The latter bands relate to positive ions since they are depressed by hole traps and enhanced by electron traps. The 390-mμ band is depressed by electron traps and hole traps alike. As a working hypothesis it may be supposed that these color centers are electrically neutral products from the recombination of positive and negative ions.

The 390- and 480-mμ bands can be characterized further by following the complete relaxation in a very soft matrix. The results for 0.05% CH_3I in 20:80 3MP–IP after 10, 30, and 60 min of isothermal relaxation appear in Figure 5. The ions responsible for 440-, 540-, and 760-mμ absorptions have decayed, while the much more slowly decaying species absorbing at 390 and 480 mμ are quite plausibly *neutral* and *metastable* since they also disappear.

To test further the tentative assignment of these two bands to a neutral recombination product, reactions 1 and 2, in which Ar is an aromatic hydrocarbon and

$$Ar^+ + I^- \longrightarrow Ar \cdot I \qquad (1)$$

$$Ar \cdot I + h\nu \longrightarrow Ar^+I^- \qquad (2)$$

$Ar \cdot I$ and Ar^+I^- the ground and optically excited states of a charge-transfer complex, were considered. Several of these were investigated by Strong, *et al.*[12] Of these, toluene and mesitylene were chosen, the complexes having λ_{max} 515 and 590 mμ, respectively. The results for 2% Ar and 0.05% CH_3I in 50:50 3MP–IP appear in Figures 6 and 7, where bands resembling those reported[12] can be seen.

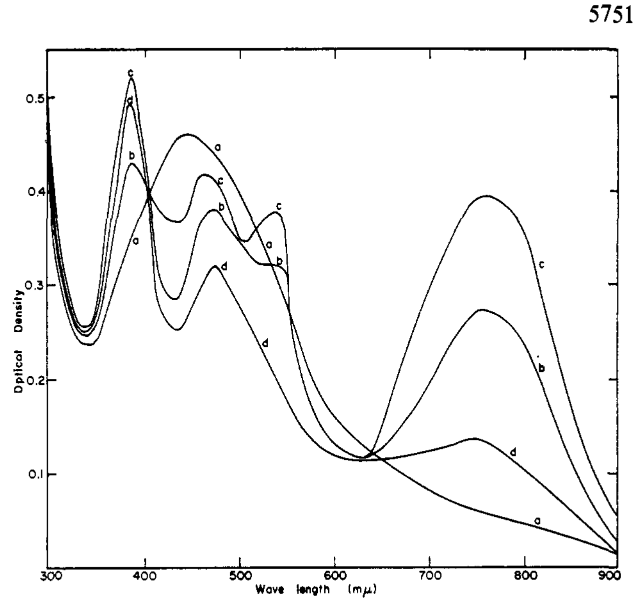

Figure 4. Methyl iodide (0.05%) in 70:30 3MP–IP at 77°K; dose 7.75 × 10^{18} ev/g: (a) immediately after irradiation; (b) same sample after 1 hr of dark decay; (c) same sample after 2 hr of total dark decay; (d) preceding sample after 75-sec bleaching with tungsten light.

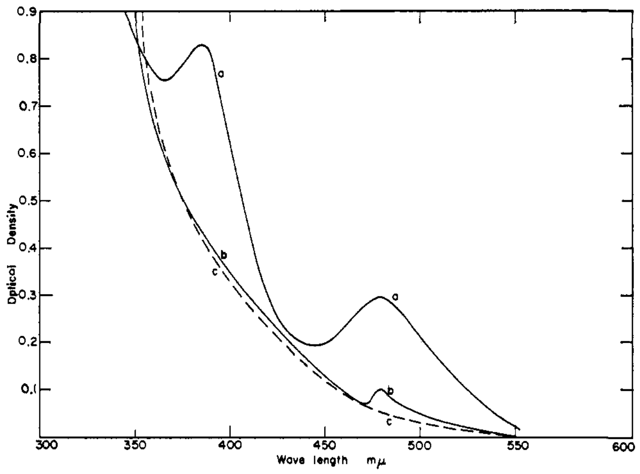

Figure 5. Methyl iodide (0.05%) in 20:80 3MP–IP at 77°K; dose 1.55 × 10^{19} ev/g: (a) immediately after irradiation; (b) after 30-min dark decay at 77°K.; (c) same after 60-min total dark decay at 77°K.

Discussion

The 440-mμ band is assigned to RI^+ for several reasons. The species responsible has positive ion character (*i.e.*, it is a positive ion or has a positive ion precursor) and decays most rapidly, indicating that it is actually an ion. Also, it is the precursor of all other transient species, it is the only one present in significant yield at small concentrations of RI, and it is not observed in pure RI.[9a] The band threshold (1.6 ev) agrees with the separation of energy levels for CH_3I^+ at 9.51 and 11.22 ev, and a 1.6-ev excitation appears for

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[12] R. L. Strong, S. J. Rand, and J. A. Britt, *J. Am. Chem. Soc.*, **82**, 5053 (1960).

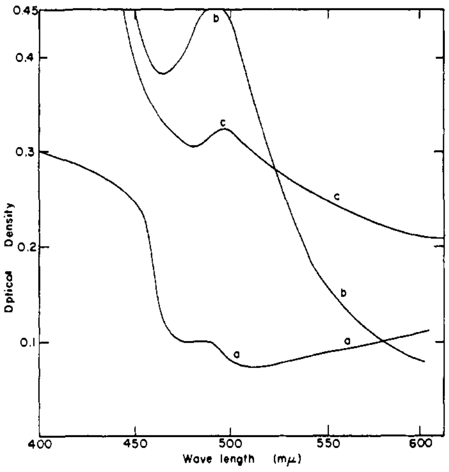

Figure 6. (a) Toluene (2%) in 50:50 3MP–IP immediately after irradiation; dose: 1.55 × 10^{19} ev/g; (b) toluene (2%) + 0.05% methyl iodide in 50:50 3MP–IP immediately after irradiation; (c) preceding sample after 2-hr dark decay at 77°K.

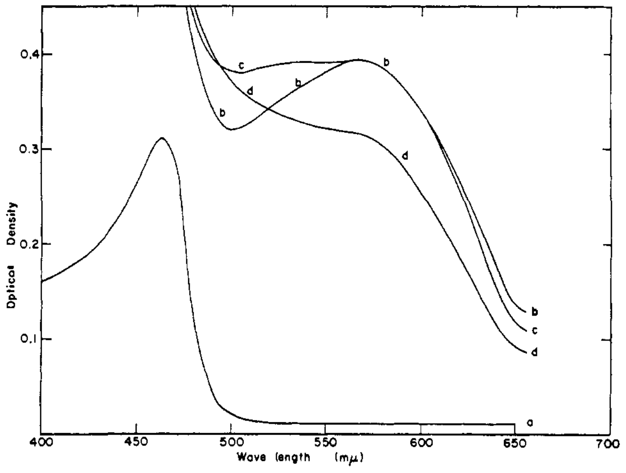

Figure 7. (a) Mesitylene (2%) in 50:50 3MP–IP immediately after irradiation; dose: 1.55 × 10^{19} ev/g; (b) mesitylene (2%) + 0.05% methyl iodide in 50:50 3MP–IP immediately after irradiation; (c) same as preceding sample after 20-min dark decay; (d) same sample after 90-min total dark decay at 77°K.

other RI^+. For CH_3I^+ these levels were assigned[13,14] to the $^2E_{1/2}$ and $^2A_1$ states, the optical excitation corresponding to promoting an electron from the σa_1 orbital of the C–I bond to the vacancy in the nonbonding $p\pi e$ orbital of I.[13] The only other possible optical transition, from the C–H orbital to the nonbonding orbital vacancy, is not observed for the assumed CH_3I^+, but the corresponding ionization potential is known.[13,14]

For seven alkyl iodides in 3MP (CH_3I alone excepted) the 360-mμ satellite of the 390-mμ band was very weak for *n*-RI (see Figure 2), somewhat stronger for *i*- and *sec*-RI, and strongest for *t*-RI.[9b] The strength of the band correlates quite well with the number of C–C bonds adjoining the I atom. The higher appearance potentials of C_2H_5I at 12.1 ev and C_3H_7I at 12.2 ev[15] (ionization potentials = 9.3), which are not matched by a similar value for CH_3I, are attributable to removal of an electron from the C–C bond.[16] We assign the optical transition at 360 mμ to an electron transfer in RI^+ from the nearest C–C bond(s) to the lone-pair vacancy. Little overlap is expected for these orbitals and the band is very weak for *n*-RI. The exception for CH_3I^+ and the comparatively high oscillator strength for *t*-$C_4H_9I^+$ are also accounted for.

Since the ions absorbing at 440 mμ, now assigned to RI^+, are precursors of the species absorbing at 390 and 480 mμ, and since the latter have both positive ion and negative ion character, decay very slowly, and are not ultimate products, we attribute their formation to the reaction

$$RI^+ + I^- \longrightarrow RI{\cdot}I \qquad (3)$$

This assignment agrees with good growth of 390-mμ absorption by isothermal relaxation and little or none by optical excitation of the precursors, as well as the insensitivity of this band to direct bleaching. For the flash photolysis of I_2 in C_2H_5I, such bands appear[17] at λ_{max} 390 and 490 mμ. We attribute this spectrum to a charge-transfer doublet. Both CH_3I^+ and $C_2H_5I^+$ have $^2P_{3/2}$ states at 9.54 and 9.34 ev and $^2P_{1/2}$ states at 10.18 and 9.93 ev, respectively.[18] The average of these doublet separations is 0.62 ev. We assume that these doublets give rise to corresponding doublet states of the optically excited complexes RI^+I^-. In the simple approximation $h\nu = I - A - C$, the Coulomb and electron affinity terms can be taken as constants for the two ionization potentials. The observed band maxima separation of the charge-transfer complexes, approximating ~0.65 ev for various RI, agree quite well with the doublet separation from spectroscopic ionization potentials.

For the tests on analogous charge-transfer complexes Ar·I, the spectra designated a in Figures 6 and 7 are assignable to $C_6H_5CH_3^+$ and $C_6H_3(CH_3)_3^+$, respectively.[19] The isothermal growth of the 490-mμ band (Figure 6) is consistent with the assumed ion recombination mechanism, forming $C_6H_5CH_3{\cdot}I$. The isothermal decay of the 570-mμ band (Figure 7) is consistent with the transient character of $C_6H_3(CH_3)_3{\cdot}I$.

The bands at 540 and 760 mμ are assigned to $(RI)_2^+$ since RI^+ (360 and 440 mμ) is a precursor and because of the concentration dependence, and for other reasons given. Their growth by isothermal relaxation from RI^+ in a soft matrix is attributable to reaction 4 induced

$$RI^+ + RI \longrightarrow (RI)_2^+ \qquad (4)$$

by mutual motion of RI^+ and I^-. Subsequent recombination by reaction 5 enhances 390–480-mμ absorption, and evidence is supplied from the work of Claridge and Willard[9b] (their Figure 4). The conversion of RI^+ to $(RI)_2^+$ by optical excitation in a hard matrix (3MP, −196°) is attributable to preexisting neutral dimer, $(RI)_2$, caused by permanent dipole pair-

$$(RI)_2^+ + I^- \longrightarrow RI{\cdot}I + RI \qquad (5)$$

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[13] D. C. Frost and C. A. McDowell, *Proc. Roy. Soc.* (London), **A241**, 194 (1957).

[14] S. Tsuda, C. E. Melton, and W. H. Hamill, *J. Chem. Phys.*, **41**, 689 (1964).

[15] S. Tsuda and W. H. Hamill, *ibid.*, **41**, 2713 (1964).

[16] K. Fueki, *J. Phys. Chem.*, **68**, 2656 (1964).

[17] T. A. Gover and G. Porter, *Proc. Roy. Soc.* (London), **A262**, 47 (1961). In Table I of this article, only the band with λ_{max} 490 mμ was reported for C_2H_5I as solvent, together with data for 16 other solvents, but Figure 1 of this article shows equal maxima at 490 and 390 mμ. There is no discussion of this doublet, and apparently all other charge-transfer bands observed were singlet.

[18] W. C. Price, *J. Chem. Phys.*, **4**, 539, 547 (1936).

[19] T. Shida and W. H. Hamill, *ibid.*, **44**, 4372 (1966).

ing. Optical excitation of RI^+ to RI^{*+} (11.22 ev for CH_3I^+, for example) permits charge transfer to and migration through 3MP (ionization potential ~10.1 ev) followed by trapping on $(RI)_2$ to form $(RI)_2^+$. Such complexes have been observed for several alkyl iodides and bromides in the mass spectrometer.[20,21] For $(C_2H_5I)_2^+$ the ionization efficiency curve can be normalized to that for $C_2H_5I^+$ throughout, except for a small but well-defined maximum at 1.5 ev above onset and a second poorly defined maximum at 2.6 ev.[22] For $(c\text{-}C_5H_9I)_2^+$ a maximum occurs at 0.9 ev, and for $(n\text{-}C_5H_{11}I)_2^+$ maxima were found at 1.0 and 1.8 ev. The average values, since none is precise, are 1.1 ev for the first and 2.2 ev for the second. These maxima correspond to vertical transitions and should be compared with $(RI)_2^+$ optical band maxima which are 1.6 and 2.3 ev.

Evidence for $RI \cdot I$ complexes, observed under various other experimental conditions, have been reported. Ebert, *et al.*,[23] observed bands at 390 and 465 mμ following pulse radiolysis of cyclohexyl iodide. The first band is attributed to $C_6H_{11}I \cdot I$, the second to I_2^-. Timm[24] observed bands at 394 and 471 mμ following photolysis of C_2H_5I in isopentane–3-methylpentane at −196° and attributed the first to HI I and the second to $C_2H_5I \cdot I$. Thomas[25] observed an unresolved band with maxima at 312 and 352 mμ following pulse radiolysis of aqueous CH_3I and postulated $CH_3I \cdot I$.

The mechanisms by which energy is transferred from the major component to a minor component of a radiolytic system have been considered frequently. The alkyl iodide–alkane system serves as a model for illustrating the chemistry to be expected from one type of system as regards ionic processes. It is of interest that radical positive ions of relatively unstable alkyl iodides can survive charge recombination with I^-. It can be inferred, then, that alkane and alkene radical ions can also survive recombination with X^- when the electron affinity is ~3 ev, or possibly less. Earlier indirect evidence had supported this interpretation,[26] based on dissipation of potential energy of the ion to its environment through electron affinity, polarization, and Coulombic energy.

The identification of charge-transfer complexes as products of ion recombination provides a useful new tool for radiation chemistry. To the best of our knowledge, the only identified products of charge recombination in radiation chemistry are those reported here and the excited species identified through recombination luminescence.[27]

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(21) A. J. Lorquet and W. H. Hamill, *ibid.*, **67**, 1709 (1963).

(22) The text appears to be in error, locating the second maximum at 3.5 ev while the figure shows the maximum at ~2.6 ev, which we use.

(23) M. Ebert, J. P. Keene, E. J. Land, and A. J. Swallow, *Proc. Roy. Soc.* (London), **A287**, 1 (1965).

(24) D. Timm, *Acta Chem. Scand.*, **20**, 2219 (1966).

(25) J. K. Thomas, *J. Phys. Chem.*, **71**, 1919 (1967).

(26) S. Z. Toma and W. H. Hamill, *J. Am. Chem. Soc.*, **86**, 1478 (1964).

(27) J. A. Leone and W. H. Hamill, *J. Chem. Phys.*, in press, and references cited.

Competitive Solvation of the Hydrogen Ion by Water and Methanol Molecules Studied in the Gas Phase

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Contribution from the Chemistry Department, University of Alberta, Edmonton, Canada. *Received May 15, 1967*

Abstract: Studies of the ions in irradiated water–methanol vapor mixtures show that the principal species are clusters, $(CH_3OH)_m(H_2O)_wH^+$. Methanol is taken up preferentially in clusters of small size. The preference for methanol decreases with size of the cluster. Water and methanol are taken up with equal preference for clusters with $m + w = 9$. Water is taken up preferentially in larger clusters. The results predict preferential solvation of the proton by water in macroclusters, *i.e.*, liquid water–methanol solutions. The preference for methanol does not show a distinct inner–outer shell behavior for clusters with $m + w \leq 6$. The data indicate that in a small cluster ($m + w = 3$, 4, or 5) the methanol molecules are equivalent among themselves, as are the water molecules. Thus the notation, $(CH_3OH)_{m-1}(H_2O)_wCH_3OH_2^+$ or $(CH_3OH)_m(H_2O)_{w-1}H_3O^+$, which indicates that the proton is more strongly bound to one particular molecule, would seem to be incorrect. Extrapolation of the data to clusters containing only the proton and one solvent molecule predict 11 kcal/mole for the difference between the proton affinity of methanol and water. This is close to estimates obtained by other means.

The interaction of ions with solvent molecules has been studied for many years in liquid solutions. More recently considerable advances in this field were made by applying the powerful techniques of nmr and esr. Starting a few years ago we have published work[1-4] in which a new approach is used, namely, the study of ion–solvent interactions in the gas phase. This approach has the very special advantage of studying ion–solvent molecule complexes (ions surrounded by a cluster of solvent molecules) without the interference of the bulk of the solvent. The method is thus specially

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(1) P. Kebarle and A. M. Hogg, *J. Chem. Phys.*, **42**, 798 (1965).

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(4) P. Kebarle in "Applications of Mass Spectrometry in Inorganic Chemistry," Advances in Chemistry Series, American Chemical Society, Washington, D. C., in press.