maintain the complex was present during isolation, forcing the reaction in eq. 1 to the left.

Thus, the mole ratio of butadiene to silver in the solid complex mixture is a function of the temperature and pressure prevailing during formation and isolation.

Heats of Dissociation.—Heats of dissociation, calculated from equilibrium data, are 10.8 and 13.0 kcal./mole, for $AgNO_3/C_4H_6(s)$ and $(2AgNO_3)/C_4H_6(s)$, respectively.

An extensive search of the literature failed to uncover any previous mention of a stable silver/butadiene complex salt, much less a mixture of two such salts, even though a number of silver/diene complex salts have been characterized.[1,4,14] However, the formation of a single complex salt, $(2CuCl)/C_4H_6(s)$, has been reported.[15,16]

Difference between the reported heat of dissociation of $(2CuCl)/C_4H_6(s)$ (17.0 kcal./mole) and that of $(2AgNO_3)/C_4H_6(s)$ (13.0 kcal./mole) can be attributed to the generally lower stability of a silver/olefin complex as compared to that of a copper/olefin complex.[17] A similar difference should exist between the heats of dissociation of the mono-metal-ion/diolefin salts. Unfortunately the formation of $CuCl/C_4H_6(s)$ has not been reported, although it is likely that, under suitable conditions, such a compound could exist. The heat of dissociation of $AgNO_3/C_4H_6$ (10.8 kcal./mole) is greater than that calculated for $AgNO_3$/1-butene (7.3 kcal./mole).[18] From this, it appears that the conjugated double bond supplies additional stabilization in complex formation. However, the nature of this stabilization is not evident from the present work.

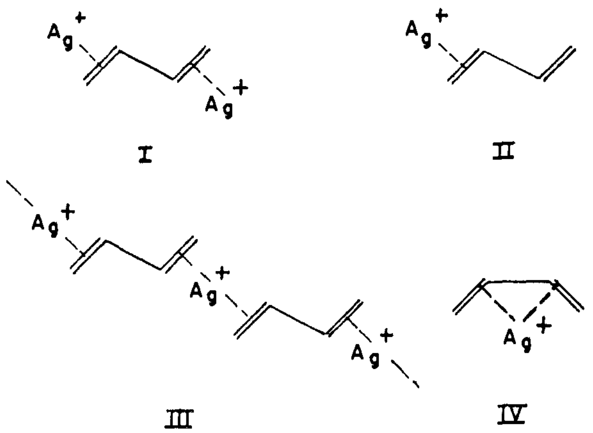

Fig. 3.

Structure of the Complex Species.—Since the butadiene molecule possesses two double bonds and it is generally accepted that these can act independently in complex formation,[19] a number of possibilities for the structures of the two complexes may be considered (Fig. 3). It may be assumed readily that the 2:1 complex has the structure I. In view of the discrepancy cited above between the heats of dissociation of the 1:1 complex and that of $AgNO_3$/1-butene, II would not appear to be a good possibility for the structure of solid 1:1. This objection may not, however, apply when this material is in solution. Structure III is similar to that proposed for a solid 1:1 $AgNO_3$/norbornadiene complex[14] and has the advantage that it would account for the ease with which interconvertibility between the 1:1 and the 2:1 complexes is accomplished in the solid phase. Such an interconversion is not readily visualized for structure IV which, however, in the absence of additional physical data, cannot be excluded and which does provide for the additional stabilization observed for the 1:1 complex.

Acknowledgment.—The authors wish to express their appreciation to Mr. R. Fischer for his able assistance with the experimental work and to Dr. E. Solomon for his valuable suggestions in preparing the manuscript.

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Effect of Electric Charge on the Reactivity of Some Isoelectronic Free Radicals[1]

BY T. FFRANCON WILLIAMS

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Calculations are presented on the energetics of hydrogen atom abstraction reactions initiated by isoelectronic free radicals derived from oxygen or nitrogen compounds. Analysis of these results leads to the concept that positively charged species are inherently more reactive. Implications are discussed and acid catalysis of some free radical reactions is predicted under suitable conditions.

Introduction

The extensive literature of free-radical chemistry is well reviewed in several recent publications[2-6] but it seems that only scant attention has been focused on an explicit comparison of the reactivity of a neutral free radical with its charged isoelectronic analogs. This neglect stems in large measure from the absence of comparative information on

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(1) The author is indebted to the Atomic Energy Commission for partial support of this contribution.

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the reactions of charged free radicals since these latter species are rarely thought to be present when radicals are generated by thermal or photochemical methods. However, it is becoming increasingly evident[7] that charged radicals are of importance in reactions initiated by ionizing radiation and, as a result of mass-spectroscopic studies,[8–11] much precise information is now available on the rates and energetics of ionic processes in the gas phase. It is the purpose of this communication to point out that the effect of charge on free-radical reactivity accords with the expected differences in activation energy for some simple reactions. The theoretical basis of such energy differences is specified and some possible, but hitherto unforeseen, implications are made apparent.

Discussion

In the following series of isoelectronic free-radical species, the neutral entity has the odd electron localized on an atom possessing at least one lone pair of electrons. This atom is electronegative with respect to hydrogen.

Series

I $\overset{+\cdot}{\mathrm{N}}\mathrm{H}_3$, $\dot{\mathrm{N}}\mathrm{H}_2$, $\overset{-\cdot}{\mathrm{N}}\mathrm{H}$, $\overset{2-\cdot}{\mathrm{N}}$ III $\mathrm{H}\overset{+\cdot}{\mathrm{F}}$, $\dot{\mathrm{F}}$

II $\mathrm{H}_2\overset{+\cdot}{\mathrm{O}}$, $\mathrm{H}\dot{\mathrm{O}}$, $\overset{-\cdot}{\mathrm{O}}$ IV $\overset{+\cdot}{\mathrm{X}}$ (X = noble gas atom)

For series I and II the neutral radical is amphoteric and thereby may gain or lose a proton to form the positive and negative ion-radicals, respectively. We shall confine attention to reactions involving hydrogen atom abstraction by the free radical from a neutral molecule as represented in (1), since such reactions have been extensively studied and are conceptually of the simplest type; moreover, they are of considerable importance throughout free-radical chemistry.

$$\mathrm{Y}\cdot + \mathrm{H{-}Z} \longrightarrow \mathrm{Y{-}H} + \mathrm{Z}\cdot \qquad (1)$$

In closely related series, a parallelism may be expected between the activation energy and the over-all thermochemical change. This principle[12] has been widely applied in discussions[13] concerning the variation of reactivity with structure. Whilst it is undoubtedly true that the repulsive energies between radical Y· and molecule H–Z, and between Y–H and Z·, also influence the energy of the transition state,[6] such considerations are less subject to reliable *a priori* evaluation as a function of the structure of radical Y·. However, insofar as neutral free radicals are concerned, there is strong evidence[5] that an increase in the electronegativity of the attacking radical contributes to a lower activation energy than would be expected on thermochemistry alone. It will be seen that this latter consideration reinforces our conclusion derived below from over-all energetics.

Let reactions 2, 3 and 4 represent hydrogen atom abstraction processes from the water molecule.[14]

$$\mathrm{H_2\overset{\cdot+}{O}} + \mathrm{H_2O} \longrightarrow \mathrm{H_3\overset{+}{O}} + \cdot\mathrm{OH} \qquad (2)$$

$$\mathrm{H\dot{O}} + \mathrm{H_2O} \longrightarrow \mathrm{H_2O} + \cdot\mathrm{OH} \qquad (3)$$

$$\overset{\cdot-}{\mathrm{O}} + \mathrm{H_2O} \longrightarrow \mathrm{O\overline{H}} + \cdot\mathrm{OH} \qquad (4)$$

The exothermicity, $-\Delta H_r^0$, of reaction 2 in the gas phase at 298°K. can be calculated conveniently from a thermochemical cycle which leads to the expression

$$-\Delta H_r^0 = I_{\mathrm{H_2O}} + P_{\mathrm{H_2O}} - I_{\mathrm{H}} - D_{\mathrm{H-OH}} \qquad (5)$$

where $D_{\mathrm{H-OH}}$ refers here to the standard enthalpy change on the dissociation of $H_2O(g)$ into H(g) and OH(g) at 298°K. and is taken[15] to be 118.8 kcal./mole. The proton affinity of a molecule, P_{M}, is defined as the heat of reaction accompanying the addition of a proton to the molecule under standard conditions in the gas phase. A value for $P_{\mathrm{H_2O}}$ equal to 182 kcal./mole is now generally accepted.[16] It was obtained by Sherman[17] from lattice energy calculations on ammonium and oxonium perchlorates, but by this method of evaluation, $P_{\mathrm{H_2O}}$ depends on a previously determined value for $P_{\mathrm{NH_3}}$ (206.8 kcal./mole), which was deduced by the same author.[17] A more recent calculation[18] of $P_{\mathrm{NH_3}}$ gives a figure of 202 kcal./mole at 298°K. so that the value of $P_{\mathrm{H_2O}}$ quoted above is probably accurate to about 5 kcal./mole. We shall use $P_{\mathrm{H_2O}} = 182$ kcal./mole and $P_{\mathrm{NH_3}} =$ 202 kcal./mole in our subsequent calculations, but the conclusions of this paper are in no way affected by the slight uncertainty in these values. The

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(7) D. P. Stevenson, *J. Phys. Chem.*, **61**, 1453 (1957), is the leading reference to this topic; also T. Ff. Williams, *Trans. Faraday Soc.*, **57**, 755 (1961); T. Ff. Williams, *Nature*, **194**, 348 (1962), and references contained therein.

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(14) It should be emphasized that the treatment and the conclusions arrived at herein are independent of the nature of the hydrogen atom donor. Thus a hydrocarbon RH could replace neutral H_2O in reactions 2, 3 and 4, whereby the energetics would then be represented by the general equation

$$-\Delta H_r^0 = I_{\mathrm{M}} + P_{\mathrm{M}} - I_{\mathrm{H}} - D_{\mathrm{H-R}} \qquad (5.1)$$

where M denotes the molecule (H_2O, OH^- and O^{2-} in 2, 3 and 4, respectively) from which the *initial* free radical is derived by ionization. Hence the only change in the energy calculations on substitution of H_2O by RH would involve an increase in the exothermicity of reactions 2, 3 and 4 by the constant increment $D_{\mathrm{H-OH}} - D_{\mathrm{H-R}}$, and the trend remains unaltered. It might be objected that the *mechanism* of the known ion-molecule reaction between $\mathrm{H_2\overset{+\cdot}{O}}$ and H_2O could conceivably involve proton transfer to the neutral H_2O rather than hydrogen atom transfer to $\mathrm{H_2\overset{+\cdot}{O}}$ as represented here. Experiment cannot distinguish between the two possibilities in this special case. However, it is known[11] with certainty that the reaction between $\mathrm{H_2\overset{+\cdot}{O}}$ (or $\mathrm{D_2\overset{+\cdot}{O}}$) and the molecules H_2, C_3H_8, *n*-C_4H_{10}, cyclo-C_3H_6, C_2H_2, NH_3 and H_2S all occur by hydrogen atom transfer so that our general approach would seem to be valid and the choice of H_2O as the neutral molecule is merely arbitrary and convenient for the later calculations of this paper.

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ionization potentials of water[11] (I_{H_2O}) and the hydrogen atom (I_H) at 298°K. are 291 kcal./mole and 315 kcal./mole, respectively, so that ΔH_r^0 for reaction 2 in the gas phase is -39 kcal.; all ΔH_r^0 values given in this paper refer to 298°K. While reaction 3 is clearly thermoneutral, calculation of ΔH_r^0 for 4 depends upon a knowledge of the electron affinity of the oxygen atom and the OH radical. Assuming[19] E(O) and E(OH) to be 53.8 kcal./mole and 50 kcal./mole, respectively, and taking[15] $\Delta \bar{H}_f^0$ (O) = 59.2 kcal./mole, $\Delta \bar{H}_f^0$ (H_2O) $= -57.8$ kcal./mole and $\Delta \bar{H}_f^0$ (OH) = 8.9 kcal./mole, ΔH_r^0 for 4 in the gas phase is derived to be $+20.2$ kcal.

For the isoelectronic series I, the calculation of ΔH_r^0 for reaction 6

$$\overset{\cdot +}{N}H_3 + NH_3 \longrightarrow \overset{+}{N}H_4 + \dot{N}H_2 \qquad (6)$$

follows from the relationship

$$-\Delta H_r^0 = I_{NH_3} + P_{NH_3} - I_H - D_{H-NH_2} \qquad (7)$$

The values[11,18–20] $I_{NH_3} = 242$ kcal./mole, $P_{NH_3} = 202$ kcal./mole, $I_H = 315$ kcal./mole and D_{H-NH_2} 106 kcal./mole lead to ΔH_r^0 for 6 in the gas phase $= -23$ kcal. A hydrogen atom transfer between $\dot{N}H_2$ and NH_3 is, of course, thermoneutral. Therefore, it is evident from the above calculations that the bond dissociation energies at 298°K. decrease in the order $D_{H-\overset{+}{O}H_2} > D_{H-OH} > D_{H-\bar{O}}$, and $D_{H-\overset{+}{N}H_3} > D_{H-NH_2}$.

Recent photoionization measurements (K. Watanabe and J. R. Mottl, *J. Chem. Phys.*, **26**, 1773 (1957)) suggest $I_{NH_3} = 234$ kcal./mole. The acceptance of this value rather than the electron impact determination quoted in the paper leads to a *minimum* of 15 kcal. for the exothermicity of reaction 6.

Now, if electronegativity is defined[21] as the tendency of an atom in a molecule to attract electrons to itself, we can *independently* proceed to examine the effect on electronegativity due to the introduction of formal electric charge on the bonding atom. The most rigorous measure of electronegativity is due to Mulliken[22] and is given by the sum of the ionization potential and the electron affinity of the atom in the valence state and therefore automatically takes into account the effect of formal charge. We shall use this quantitative method for the univalent atoms I· and $\overset{\cdot +}{Xe}$ below, but for the more complicated cases of oxygen in H_3O^+, H_2O, OH^-, and nitrogen in $\overset{+}{N}H_4$ and NH_3, we shall have to invoke more qualitative arguments, but these are nonetheless convincing. Pauling[21] estimated the change in electronegativity of nitrogen in going from NR_3 to $\overset{+}{N}R_4$ solely in terms of the expected increase in effective nuclear charge, and he concluded that the electronegativity of nitrogen was thereby increased by about 2/3 of the difference between the values for neutral nitrogen and oxygen atoms. Conversely, by the same argument, the electronegativity is decreased by the presence of formal negative charge. An equivalent description[23] is that the increase in electronegativity of the oxygen atom within series II results from a proportional decrease in the lone-pair charge around the oxygen nucleus as one and two protons are added to $\overset{\cdot -}{O}$ to from $\dot{O}H$ and $\overset{\cdot +}{O}H_2$, respectively. Finally, the conclusion that the electronegativity of the central atom (N,O) is greater in the positively charged ions (NH_4^+, H_3O^+) relative to the neutral molecules can be clearly seen by considering the ground-state electronic structure of the ion-radicals (molecule-ions), $\overset{+\cdot}{N}H_3$ and $H_2\overset{+\cdot}{\ddot{O}}$; in each case the major valence bond structure corresponds to the loss of a non-bonding electron[24] with the result that the positive charge is in fact highly localized on the nitrogen and oxygen atoms, respectively. Hence the screening of the nuclear charge is considerably reduced and stronger bonds are formed in consequence. Thus it is consistent that the trends in bond dissociation energies reported above are in complete accord with electronegativity differences as evaluated by this alternate approach. Further, we feel confident that insofar as the relationship between electronegativity and bond energy is a fundamental axiom of modern chemistry, our thesis has wide validity.

The generality of the effect we describe is also borne out by a comparison of the reactivity of noble gas ions with their isoelectronic halogen atom countertypes. Recent work[25] has shown that $\overset{\cdot +}{Xe}$ reacts with methane to form XeH^+ and $XeCH_3^+$, whereas hydrogen atom abstraction by the neutral iodine atom from hydrocarbons is rarely encountered due to the high activation energy involved. The electronegativity of ground state $\overset{\cdot +}{Xe}$ given by the Mulliken formula[22]

$$\chi_{\dot{X}e^+} = I_{\dot{X}e^+} + E_{\dot{X}e^+} \qquad (8)$$

may be obtained from the identity

$$\chi_{\dot{X}e^+} = (A_{Xe^{++}} - I_{Xe}) + I_{Xe} = A_{Xe^{++}} \qquad (9)$$

where $A_{Xe^{++}} = 747$ kcal./g.-atom and represents the measured appearance potential[11] of Xe^{++} from gaseous xenon. Converting to the Pauling scale,[21] $\chi_{\dot{X}e^+} = 5.7$ units and hence $\overset{\cdot +}{Xe}$ is considerably more electronegative than the neutral iodine atom (2.5 units) and even exceeds that of fluorine (4.0 units).

The ion-molecule reactions of alkyl iodides[26] whereby $RI^{+\cdot}$ ions react to form the even-electron ions RI^+H and R_2I^+ illustrate the increased reactivity of the iodine atom bearing an appreciable fraction of unit positive charge.[24] While the rates of ion-molecule reactions are magnified by larger "collision" cross-sections relative to collisions between neutral species, the large probability of reaction upon every encounter in the former case can only be attributed to the negligible activation energies of such reactions which must in turn be largely determined by favorable over-all energetics. Thus endothermic ion-molecule reactions appear

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to be non-observable under mass-spectrometric conditions at energies close to the threshold of the primary ion. If the argument presented herein is valid, it would suggest that *negative* ion-molecule reactions involving hydrogen atom abstraction to a negatively charged nitrogen or oxygen atom are energetically less likely than a corresponding hydrogen atom transfer to a neutral radical. The literature reveals that such negative ion-molecule reactions involving $\overset{\cdot -}{O}$ have not been observed.[11] The only circumstance we can visualize whereby this conclusion may be vitiated is as a result of a long-lived interaction between a negative ion and a molecule held together by polarizability effects or, more likely, by ion–permanent dipole attraction until the "complex" has gained sufficient energy by thermal interchange to cross the activation energy barrier. In solution this type of effect would correspond to a form of preferential solvation of the ion by the reactant.

There is now abundant mass-spectroscopic evidence[11] for reactions involving hydrogen atom transfer from a neutral molecule to a wide variety of positively charged radicals (molecule-ions) derived from oxygen, nitrogen and halogen compounds by loss of a non-bonding electron. The general implication of such reactions for macroscopic radiation chemistry has been widely discussed,[7] but it is instructive for the purposes of this discussion to consider reaction 2 as an equilibrium in aqueous solution. Since[15] $\Delta H_{\text{hydration}}{}^0$-$(H_2O) = -10.5$ kcal./mole and $\Delta H_{\text{hyd}}{}^0\ (OH) = -6.9$ kcal./mole, $\Delta H_r{}^0$ for reaction 2 in aqueous solution is -35.4 kcal. on the reasonable assumption that the hydration enthalpies for $H_2\overset{\cdot +}{O}$ and H_3O^+ are similar in magnitude. From the values[27] for the gaseous standard entropies, $\bar{S}^0(OH) = 43.9$ cal./mole deg., $\bar{S}^0(H_2O) = 45.1$ cal./mole deg., and the entropies of hydration $\Delta S_{\text{hyd}}{}^0(OH) = -25$ cal./mole deg., $\Delta S_{\text{hyd}}{}^0(H_2O) = -28.4$ cal./mole deg., we obtain $\Delta S^0 = 2.2$ cal./mole deg. for reaction 2 in aqueous solution by making the plausible assumption $\bar{S}^0\ (H_3O^+,\ aq) \cong \bar{S}^0\ (H_2\overset{\cdot +}{O},\ aq)$. Hence ΔF^0 for reaction 2 in the aqueous phase at 298°K. is *ca.* -36 kcal. which corresponds to an equilibrium relationship of activities, $a_{H_2\overset{\cdot +}{O}} \cong 10^{-25}\ a_{OH}$, under conditions where $a_{H_3O^+} = a_{H_2O}$. As reaction 2 is known[28] to have an exceedingly high rate constant in the gaseous phase, the above line of reasoning suggests that $H_2\overset{\cdot +}{O}$ is unlikely to have any chemical significance except as the precursor of the OH radical in the radiation chemistry of aqueous solutions; this conclusion is at variance with views[29] that have been expressed elsewhere as to the persistence of "positive holes" and their supposed reactivity with dissolved solutes in irradiated water.

Our concern in the remainder of this article is to ponder upon whether the reactions of ion-radicals similar to the ones we have described here have any significance for areas of chemical kinetics beyond the confines of radiation chemistry. One conclusion follows simply from the above analysis: that even in strongly acidic *aqueous* solutions containing OH radicals, the $H_2\overset{\cdot +}{O}$, OH acid–base equilibrium is so overwhelming in favor of the neutral radical that $H_2\overset{\cdot +}{O}$ is unlikely to be formed. However, although the protonation of neutral free radicals derived from nitrogen or oxygen compounds is thermodynamically unfavorable in aqueous systems, it is suggested that such protonation may conceivably, or even readily, occur in strongly acidic non-aqueous media. Thus neutral radicals such as $R\dot{O}$, $R\dot{O}_2$, $\dot{N}R_2$ and $\dot{C}l$, which oftentimes are important intermediates in chemical reactions, would become much more potent in hydrogen atom abstraction when converted to their protonated forms, $R\overset{+\cdot}{O}H$, $R\overset{+\cdot}{O}_2H$, $\overset{+\cdot}{N}R_2H$ and $H\overset{+\cdot}{C}l$. The best homogeneous media for the realization of this increased reactivity would be expected to include concd. sulfuric acid, BF_3–HF and similar examples of highly acidic solutions.[30] It may also be pertinent to remark that free-radical protonation may occur on Brönsted-acid sites located on solids in heterogeneous reactions and this could possibly contribute to the well-known catalytic properties of these solids in some specific cases. In combustion processes, the conversion of $R\dot{O}_2$ and $H\dot{O}_2$ to $R\overset{+\cdot}{O}_2H$ and $H_2\overset{+\cdot}{O}_2$ should result in accelerated rates since the neutral species tend to be sluggish in chain transfer with hydrocarbons.

At this point, I am indebted to the referee of this paper for directing my attention to a possible example[31] of the effect we seek to describe. Corey and Hertler[31] have demonstrated that the acid-catalyzed reactions of N-haloamines proceed through free-radical intermediates, and the evidence suggests the participation of aminium ion-radicals $R_2\overset{+}{\dot{N}}H$ in intramolecular hydrogen atom transfer as the propagation step. The phenomenon of acid catalysis in this system may be explained[31] in terms of increased reactivity in propagation and/or slower termination of radical recombination. Corey and Hertler conclude that, "whether the aminium radical is especially effective in removing H from C (relative to a neutral N radical) also must remain unanswered for the present; however, this is not an unlikely possibility."

While some of the remarks in this last section are necessarily speculative at this stage, the main contention of this paper is that there are sound theoretical reasons for expecting acid catalysis of some free radical reactions to apply in suitable circumstances.

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(30) Thanks are tendered to the referee for some useful suggestions.

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Stable positive ion-radicals derived from *p*-phenylenediamine (Würster salts) are well known (L. Michaelis, M. P. Schubert, and S. Granick, *J. Am. Chem. Soc.*, **61**, 1981 (1939)) where the odd electron is *delocalized* over the entire molecule. It follows that the considerations developed herein are inappropriate to this special case.

In sulfuric acid, equilibria of the type represented by $HSO_4^- + R\overset{+\cdot}{O}H \rightleftarrows S\dot{O}_4^- + ROH_2^+$ probably play an important role in determining the ultimate nature of radicals generated in the system (*cf.* M-T. Tsao and W. K. Wilmarth, *Disc. Faraday Soc.*, **29**, 137 (1960)).