

Formation of Dimer Cations of Aromatic Hydrocarbons

STABLE molecules and inert gas atoms, M , form "unstable" dimers, M_2 , which are held together only by van der Waals forces. When the dimer is ionized, an anti-bonding electron is removed and the species M_2^+ should be stable with respect to $(M^+ + M)$. Such species have long been known for $M =$ inert gas (dissociation energy, D , ~ 1 eV) and $M = N_2$, CO, etc. ($D \sim 0.5$ eV). Dimer cations of derivatives of naphthalene¹⁻³, anthracene^{1,2} and benzene³ have recently been detected by electron spin resonance (e.s.r.)^{1,2} and optical absorption spectroscopy³. The e.s.r. evidence^{1,2} suggests that the dimer cations have symmetrical sandwich structures similar to those postulated for excimers, M_2^* (ref. 4). These species may be formed by reaction (1) whenever the monomer ions are produced chemically, by high energy radiation, or by electrolysis.



Our aim here is to assess the possible importance of these species in solution at room temperature, by estimating the equilibrium constant, K , of (1), for a number of compounds.

These species have a strong absorption band in the red or near infrared³ due to the transition between the attractive ground state and the repulsive excited state of M_2^+ formed by in phase and out of phase combination of the wave-functions corresponding to charge exchange, $\psi(A^+)\psi(B) \pm \psi(A)\psi(B^+)$, where A, B represent the component molecules. If the splitting between these states is symmetrical about the initial energies of the separated molecules, then the dissociation energy, $D(M^+ - M)$, is equal to half the energy of the observed transition. It seems reasonable to suppose that the entropy change of (1) is the same as that of excimer formation



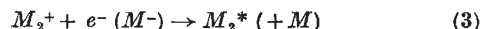
To obtain the values of K for reaction (1) at 20° C given in Table 1, values for reaction (2) have been multiplied by $\exp\{[D(M^+ - M) - D(M^* - M)]/RT\}$. These values should be regarded as upper limits of K for two reasons. First, half the transition energy is probably an over-estimate of $D(M^+ - M)$; second, the tighter binding found in most M_2^+ compared with M_2^* will lead to a lower entropy in M_2^+ . If $[M] \gg [M^+]$, $[M_2^+]$, the results show that dimer cation formation must occur in fairly dilute solutions and this form will predominate in concentrated solutions or in the pure liquids.

This type of binding can, of course, produce larger clusters such as M_3^+ . If one assumes a triple sandwich structure then a Hückel molecular orbital calculation gives a total binding energy of $\sqrt{2}\beta$ while that of the dimer is β : the equilibrium constant for formation of M_3^+ from M_2^+ will then be 10^5 – 10^6 times smaller than for (1). M_3^+ will probably be formed only in very strong solutions and pure liquids while concentrations of larger clusters will be negligible.

The formation of dimer cations will probably affect the reactions of the ions: that is to say, it will slow down the transfer of charge between like molecules in solution and so lead to ion-recombination before charge can be

transferred to additives. This will alter the chemical and scintillation properties of solutions exposed to high-energy radiation. The dimer cations may undergo specific reactions themselves; they have been postulated as intermediates in the oxidative oligomerization of carcinogenic hydrocarbons⁸—possibly an important step in carcinogenesis.

On recombination, dimer cations will probably give excimers



This has been observed at low temperatures³ but may not occur at room temperature if a repulsive excimer state is the first product. Recombination of M^+ and M^- does not give M_2^* at low temperatures³ and the same result may be found at room temperature for electron transfer even in polar solvents is believed to take place over distances greater than 10 Å (ref. 9). Excimer emission in electrochemiluminescence¹⁰ may be due at least in part to reaction (3). An important result of reactions (1) and (3) in radiation chemistry is that the relative yields of singlet and triplet states are likely to be altered. In irradiated non-polar liquids, ion lifetimes are very short¹¹ so that M_2^+ formation will depend on the rate of the forward reaction, which is probably diffusion-controlled, rather than on the equilibrium constant.

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BIOLOGICAL SCIENCES

Disappearance of Polyribosomes during *in vivo* Erythroid Maturation and Nuclease Activity

DEBELLIS and I have compared the disappearance of ribosomes and polyribosomes during the maturation *in vivo* of erythroid cells in the rabbit¹. This involved injecting twice labelled cells, obtained from a donor animal, into a recipient animal in which the bone marrow was repressed by continuing injections of colchicine. The events which occurred, including disappearance of total erythroid cell RNA, of reticulocytes, and of ribosomes and polyribosomes, were the result of maturation of the donor cells in the recipient circulation, for evidence was presented to show that the donor cells were not removed from the circulation during the time of the study. In contrast to previous work²⁻⁴ there was no disproportionate loss of polyribosomes during erythroid cell maturation. Rowley⁵ criticized these studies because the initial and subsequent sucrose density gradient centrifugation patterns of ribosomes (Fig. 1, upper) resembled those obtained by other workers^{6,7} with polyribosomes treated with small amounts of ribonuclease. He concluded that "the similarity in (sucrose density gradient) patterns

Table 1. DISSOCIATION ENERGIES, D , AND FORMATION CONSTANTS, K , OF EXCIMERS AND DIMER CATIONS

Compound	Excimer		Dimer cation	
	D kcal mole ⁻¹	K l. mole ⁻¹	D kcal mole ⁻¹	K l. mole ⁻¹
Benzene	5.1*	0.12*	14.8	2.2×10^6
Toluene	3.9*	0.055*	13.7	1.1×10^6
Mesitylene	2.8*	0.018*	13.7	1.2×10^6
Naphthalene	5.8†	0.72‡	13.7	6.1×10^6
1,3-Dimethyl-naphthalene	6.2†	0.61‡	10.8	1.5×10^6
2,6-Dimethyl-naphthalene	6.0†	0.61‡	12.3	3.2×10^6
Pyrene	9.2‡	1,500‡	10.2	8×10^6

*, †, ‡, Data from refs. 5, 6 and 7, respectively