Radical Cations: Photochemical and Ferric Ion-induced Formation and Reactions of Indene Radical Cation

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Summary Charge-transfer excitation of complexes of anhydrides with indene or 1,1-dimethylindene in polar solvents leads to cyclobutadimerization *via* radical cations; the same products are formed using pyrylium salts as photosensitizers, as well as from the thermal oxidation; with ferric chloride; these reactions are quenchable with efficient electron donors.

Recently we reported[1] reactions of the electronically excited charge-transfer (c.t.) complexes of anhydrides with electron-rich olefins, *e.g.*, indene and benzofuran, in non-polar media, which led to oxetan formation.

It is known that exciplexes and excited c.t. complexes tend to dissociate in polar media into solvated radical ions.[2] In acetonitrile, end absorption due to c.t. complexes similar to that in benzene was observed in the above-mentioned systems. This communication describes the photoreactions of these complexes in polar solvents.

In contrast to the reaction in benzene, c.t. excitation of the complexes of dimethylmaleic anhydride (**1a**) (0·2 M) with indene (**2a**) or with 1,1-dimethylindene (**2b**) (1·0 M) in acetonitrile led to the *anti*-head-to-head cyclobutane dimer of (**2a**) and (**2b**), respectively, as the major product. These dimers are also the major products of the photoreaction of (**2a**) and (**2b**) with triplet sensitizers.[3] In the reactions of the complexes of (**1a**) with (**2a**) or (**2b**) a triplet mechanism could be excluded because in the presence of a triplet sensitizer, these reactants yield mixed cyclobutane adducts.[1,4] No detectable amounts of the dimers were formed in these triplet-sensitized reactions.

Similarly, excitation of the c.t. complexes of phthalic anhydride (**1b**) with (**2a**) or (**2b**) in acetonitrile or nitromethane yielded the same dimers as in the reactions with (**1a**). Here too a triplet mechanism could be ruled out. Addition of tetrachloroethylene (1·0 M), which is known[5] to react efficiently with triplet indene, to the above mixtures of (**2a**) or (**2b**) (1·0 M) and (**1b**) (0·1M) did not result in any significant quenching of the dimerization. The ratio of the formed dimer to the mixed adduct of (**2a**) or (**2b**) and tetrachloroethylene was $> 98:2$ whereas the corresponding ratios from the benzophenone sensitized reactions using the same concentrations and the same solvent were 5:95 and 3:97, respectively.

These results are best explained in terms of a mechanism analogous to that proposed by Ledwith[6] for *N*-vinylcarbazole dimerization. This mechanism would involve an electron-transfer reaction resulting in formation of indene radical cation ($D\cdot^{+}$) which adds electrophilically to another indene molecule, followed by a back electron transfer to the dimeric radical cation ($D\cdot\text{–}D^{+}$) and subsequent cyclization to the cyclobutane dimer (D_2).

The radical cations of (**2a**) and (**2b**) were also formed using pyrylium salts as photosensitizers. 2,4,6-Triphenylpyrylium tetrafluoroborate (**3**) ($E_T = 53$ kcal/mol)[7] is not expected to be an efficient triplet sensitizer for (**2a**) ($E_T =$ *ca.* 60 kcal/mol).[3a] Moreover, (**2a**) and (**2b**) react at a nearly diffusion controlled rate with the singlet excited state of (**3**), as indicated from fluorescence–quenching experiments. Irradiation of an acetonitrile solution of (**3**) (0·003 M) and (**2a**) or (**2b**) (1·0 M) at the longest-wavelength band of (**3**) (λ: 436 nm) yielded, however, the cyclobutane dimers of (**2**).† Addition of (**1a**) to the reaction mixture did not affect the quantum yield of dimerization and did not lead to mixed adduct formation. This further confirms that no triplet mechanism is involved in this reaction.

Analogously to the work of Ledwith,[6] the pyrylium salt sensitized dimerization of (**2b**) is enhanced in the presence of oxygen as compared to the reaction in degassed solutions. On the other hand, the quantum yield of the dimerization of (**2b**) induced by c.t. excitation of the complex with (**1b**) is not affected by degassing.

The dimerization of (**2b**) *via* the radical cation could also be achieved by oxidation with ferric chloride in acetonitrile. Besides the cyclobutane dimer, *cis*- and *trans*-1,2-dichloro-3,3-dimethylindanes and a monochlorodimethylindane were formed.

Dimerization *via* the radical cation seems to be more stereospecific than that *via* the triplet state. Whereas all four isomeric cyclobutane dimers of (**2a**) are formed in the triplet-sensitized reaction[3a] only the head-to-head dimers (*syn*: *anti* = 3: 97) are formed in the anhydrides or pyrylium salt sensitized reactions. Similarly both *anti* head-to-head and *anti* head-to-tail dimers of (**2b**) are formed in the triplet-sensitized reaction[3b] but only the former is obtained *via* the radical cation (photochemically or Fe^{3+} induced).

The dimerization of (**2b**) in the reaction with (**1b**), (**3**), or $FeCl_3$ could be quenched with compounds having lower oxidation potential than that of (**2b**), as electron transfer from the quencher (Q) to the radical cation ($D^{\cdot+}$) would be exothermic. The quenching efficiency Φ_0/Φ of the dimerization of a 0·5 M solution of (**2b**) ($+E_{1/2}$ = 1·68 V)‡ in the reaction with (**1b**) ([Q] = 10^{-3} M) increases from 2·9 to 7·2 to 9·5 with decreasing oxidation potential of (Q)[8]: 1,2-dimethoxybenzene (1·45 V), 1,4-dimethoxybenzene (1·34 V), and 1,2,4-trimethoxybenzene (1·12 V), respectively.

(*Received*, 15*th June* 1973; *Com.* 852.)

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† In the reaction with (**2a**), oligomers were also formed in addition to the cyclobutane dimers. This was not the case with (**2b**).

‡ The half-wave oxidation potential of (**2b**) was determined under similar conditions to those used for methoxybenzenes.[8] We thank Dr. G. Popp of these Laboratories for these electrochemical measurements.

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