The Effect of the Carbonyl Group, Phenyl Ring, and Ring Size of α-Iodo Cycloketones on the Nature of the Photochemical Carbon-Iodine Bond Cleavage

Boris ŠKET* and Marko ZUPAN
Department of Chemistry and Jožef Stefan Institute, Edvard Kardelj University, Ljubljana, Yugoslavia

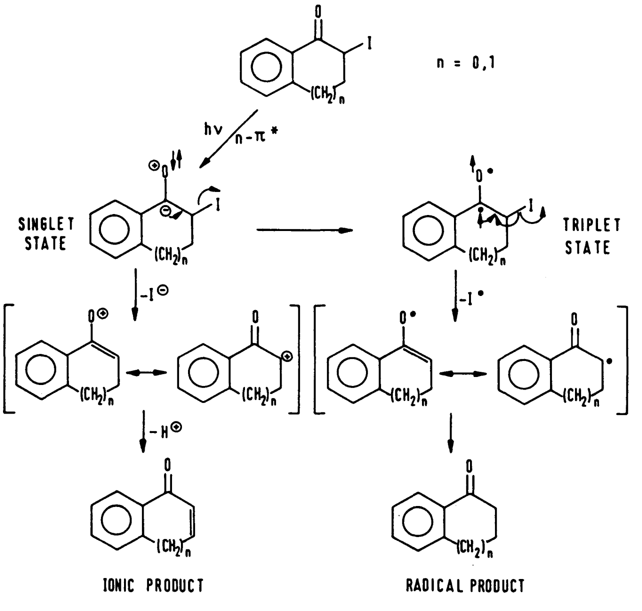
(Received October 7, 1986)

Synopsis. UV irradiation of 2-iodo-3,4-dihydro-1(2*H*)-naphthalenone and 2-iodo-1-indanone has been found to involve competing radical and ionic photoprocesses. The carbonyl group, phenyl ring and ring size of cycloketones have an influence on the nature of the photochemical carbon-iodine bond cleavage.

The photochemistry of alkyl halides$^{1)}$ and cycloalkanones$^{2)}$ has been extensively studied, but little attention has been paid to the study of α-halo cycloalkanones. There are a few reports on the study of the photochemistry of α-halo cycloalkanones which include different types of photoprocesses, such as α-cleavage,$^{3)}$ photoelimination,$^{4)}$ hydrogen abstraction by α-keto radicals,$^{5)}$ and rearrangement.$^{6)}$ The nature of the photochemical carbon-halogen bond cleavage mainly depends on the hybridization of the carbon atom, on the type of the halogen bonded, the solvent polarity and the used wavelength. It has been generally observed that by the irradiation of alkyl halides, the ratio of ionic to radical products is substantially larger for iodides than for bromides,$^{1)}$ while this tendency becomes reversed when the halogen atom is bonded to an olefinic carbon.$^{7,8)}$

It is known from literature that the irradiation of iodocyclohexane$^{9)}$ in nonpolar solvents, or even in methanol, resulted in the formation of cyclohexene as the product derived from the carbocationic intermediate and only a low percentage of cyclohexane as the radical product was observed. On the other hand, the irradiation of 2-iodocyclohexanone$^{5)}$ undergoes both ionic and radical photoprocesses, with the ratio between radical to ionic products 3.16 : 1. The mentioned results show that the photochemistry of carbon-iodine bond is greatly influenced by the α-keto group.

As the formation of α-keto carbonium ions depends on the α-halogen atom, the ring size of the ketone and the other functional groups present in the molecule, we found it reasonable to study the influence of another chromophore (phenyl ring), which is in conjugate position with the carbonyl group as also the



n	Solvent	λ/nm	% Conversion	Radical	:	Ionic	Product
0	*c*-C_6H_{12}	253.7	83	68	:	32	= 2.1 : 1
1	*c*-C_6H_{12}	253.7	100	43	:	57	= 1 : 1.32
0	CH_3COCH_3	253.7	100	100	:	0	
1	CH_3COCH_3	253.7	100	81	:	19	= 4.26 : 1
1	*c*-C_6H_{12}	300	100	48	:	52	= 1 : 1.08
1	CH_3COCH_3	300	68	73	:	27	= 2.7 : 1
1	*c*-C_6H_{12} Saturated with oxygen	253.7	72	36	:	64	= 1 : 1.78

Scheme 1. The effect of the ring size on the nature of the carbon-iodine bond cleavage.

influence of the ring size of cycloketone on the behavior of excited states of α-iodo cycloalkanones.

Irradiation of 2-iodo-3,4-dihydro-1(2*H*)-naphthalenone[10] in cyclohexane solution resulted in two products: 3,4-Dihydro-1(2*H*)-naphthalenone and 1-naphthol in the ratio 1 : 1.32 (Scheme 1). The formation of the reduction product corresponds to the radical reaction pathway, while 1-naphthol formation can be explained as a tautomer of the initially formed ionic product. On irradiation, iodine atom liberated on homolytic fission of C–I bond prefers to combine with another iodine atom than to undergo hydrogen abstraction, which is known to be extremely slow.[11] The quantity of liberated iodine corresponds to the quantity of the radical products formed, which was determined by iodine titration. 3,4-Dihydro-1(2*H*)-naphthalenone is, in the presence of iodine, under the same reaction conditions photostable and does not undergo phototransformation to 1-naphthol. Irradiation at λ=300 nm only slightly influenced the ratio of the products formed (Scheme 1). A comparison of the ratio of the radical to the ionic products formed by irradiation of 2-iodocyclohexanone (3.1 : 1) and 2-iodo-3,4-dihydro-1(2*H*)-naphthalenone (1.32 : 1) in cyclohexane solution shows that the conjugation of the carbonyl group with the phenyl ring lowers this ratio.

To understand the nature of the excited states involved, we carried out the reaction in acetone, which is a triplet sensitizer, and noted a significant change in the ratio of the radical to the ionic products (4.26 : 1). This result indicates that the solvent acetone strongly favoured the formation of the radical product. The quenching studies carried out, using oxygen as the triplet quencher, show a slight decrease in the radical product formation and a lower conversion of the starting α-iodo ketone was observed (Scheme 1).

In order to compare the influence of the phenyl group and the ring size of the cycloketone, we carried out the photoreaction of 2-iodo-1-indanone. Fifteen-hours irradiation of the indanone at λ=253.7 nm in cyclohexane resulted in a crude reaction mixture containing two products: 1-Indanone as the radical product and 2-inden-1-one[12] as the ionic product in a ratio of 2.1 : 1, while irradiation of the acetone solution under the same reaction conditions led to a complete conversion of the starting material with only 1-indanone formation (Scheme 1). On the other hand, irradiation of 2-iodo-1-indanone in methanol at λ=300 nm resulted in the formation of 2-methoxy-1-indanone (27%)[13] as ionic and 1-indanone (73%) as the radical product. The photoprocess in cyclohexane using triethylamine resulted in a marked decrease of conversion of the starting α-iodo ketone (26% conversion).

From the above results several conclusions can be derived: (i) The photochemistry of the carbon–iodine bond is greatly influenced by the α-keto group. (ii) The phenyl ring in a conjugate position with the carbonyl group has an influence on the excited states of the α-iodo cycloalkanones. (iii) The ratio between the radical and the ionic products depends on the ring size of cycloketone; the five-membered ring favours the expulsion of the iodine atom, while in the six-membered ring the expulsion of the halide anion is preferential, which can be explained by the geometry of the excited state, being, by its partially negative charge on the carbonyl carbon atom, more stabilized in the conformation of the six-membered ring[14] than in the nearly planar five-membered[15] system in α-indanone. (iv) Reaction rate of the six-membered cycloalkanone in a cyclohexane solution is larger than that of the five-membered compound. (v) The results of the quenching and sensitizing experiments indicate that the radical processes may occurr mostly through n-π^* triplet states and the ionic through singlet states, which clearly supports the Wagner model.[16]

Experimental

Irradiation was carried out in a Rayonet Photochemical Chamber, Reactor Model RPR-100 with RPR 253.7 nm and RPR 300 nm lamps. IR spectra (KBr disc) were recorded by using a Perkin-Elmer 257 spectrometer, ^{1}H NMR spectra were determined by a JEOL JNM-PS-100 in CCl_4 solution with Me_4Si as an internal standard and mass spectra were recorded on a CEC 21-110 spectrometer. Gas liquid chromatography was carried out on a Varian Aerograph Model 1800 and preparative TLC on Merck-PSC-Fertigplatten Kieselgel F 254. Melting points were determined on a Kofler apparatus and are uncorrected.

2-Iodo-1-indanone and 2-iodo-3,4-dihydro-1(2*H*)-naphthalenone[10] were prepared by iodination of the 1-indanone and 3,4-dihydro-1(2*H*)-naphthalenone in acetic acid using poly[styrene-co-4-vinylpyridinium dichloroiodate (I)].

2-Iodo-1-indanone: IR 710, 1260, 1600, 1710 cm^{-1}, ^{1}H NMR (CCl_4) δ=3.45 (1H, dd, J_{AB}=18 Hz, $J_{2,3A}$=3 Hz, H-3A), 3.90 (1H, dd, J_{AB}=18 Hz, $J_{2,3B}$=7.5 Hz, H-3B), 4.92 (1H, dd, $J_{2,3B}$=7.5 Hz, $J_{2,3A}$=3 Hz, H-2), 7.50 (4H, m, aromatic H's), mass spectra *m/z* (relative intensity): M$^+$ 258 (100), 131 (88), 127 (23), 103 (84), 102 (35), 77 (61). Found: *m/z* 257.9550, Calcd for C_9H_7IO: M, 257.9544. Mp 68—70 °C (from ethanol).

General Procedures: An 18-ml, 0.028 M (1M=1 mol dm^{-3}) solution of the 2-iodo-1-indanone or 2-iodo-3,4-dihydro-1(2*H*)-naphthalenone was irradiated in a quartz tube for 15 h, the solvent was evaporated in vacuo, the crude reaction mixture was analyzed by ^{1}H NMR and the products from irradiations outlined in Scheme 1 were isolated by preparative gas chromatography (FFAP 30% on Chromosorb AW) or preparative TLC (SiO_2, benzene), whose spectral properties agreed with those of authentic samples.

To measure the reactivity difference, 18 ml of 0.028 M cyclohexane solution of the 2-iodo-1-indanone or 2-iodo-3,4-dihydro-1(2*H*)-naphthalenone was irradiated at λ=253.7 nm and 25 °C in a quartz tube for 3 and 5 h and the degree of conversion of the starting α-halo ketone determined from the ^{1}H NMR spectrum of the crude reaction mixture.

References

1) P. J. Kropp, *Acc. Chem. Res.*, **17**, 131 (1984).

2) a) J. C. Dalton and N. J. Turro, *Ann. Rev. Phys. Chem.*, **21**, 499 (1970); b) N. J. Turro, J. C. Dalton, K. Dawes, G. Farrington, R. Hautala, D. Morton, M. Niemczyk, and N. Schores, *Acc. Chem. Res.*, **5**, 92 (1972).

3) H. G. Ferguson, P. De Mayo, F. L. M. Pattison, and T. Tabata, *Can. J. Chem.*, **41**, 2099 (1963).

4) G. Hüppi, F. G. Eggart, S. Iwasaki, H. Wehrli, K. Schaffner, and O. Jeger, *Helv. Chim. Acta*, **49**, 1986 (1966); G. Jones II and L. P. Mc Donnell, *J. Am. Chem. Soc.*, **98**, 6203 (1976).

5) P. C. Purohit and H. R. Sonowane, *Tetrahedron*, **37**,

873 (1981).

6) B. E. Kaplan and A. L. Hartwig, *Tetrahedron Lett.* **1970**, 4855.

7) B. Šket and M. Zupan, *J. Chem. Soc., Perkin Trans. 1,* **1979**, 752.

8) T. Kitamura, S. Kobayashi, and H. Taniguchi, *J. Org. Chem.*, **47**, 2323 (1982).

9) P. J. Kropp, J. A. Sawyer, and J. J. Snyder, *J. Org. Chem.*, **49**, 1583 (1984).

10) C. L. Stevens, J. J. Beereboom, and K. G. Rutherford, *J. Am. Chem. Soc.*, **77**, 4592 (1955).

11) W. V. Sherman, *Adv. Free Radical Chem.*, **3**, 50 (1969).

12) P. H. Lacy and D. C. C. Smith, *J. Chem. Soc. C,* **1971**, 41.

13) J. C. Arnould and J. P. Pete, *Tetrahedron,* **31**, 815 (1975).

14) K. Gatto, J. D. Reinheimer, K. Shafer, and J. T. Gerig, *Org. Magn. Reson.*, **6**, 577 (1974).

15) J. B. Lambert and F. R. Koeng, *Org. Magn. Reson.*, **3**, 389 (1971).

16) P. J. Wagner, *Topics in Current Chemistry,* **66**, 1 (1976).