COMMUNICATION

ChemComm
www.rsc.org/chemcomm

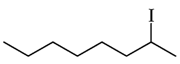
The multiphoton photochemistry of 2-iodooctane in methanol†

Fang Gao, Robert N. Compton and Richard M. Pagni*
Department of Chemistry, University of Tennessee, Knoxville, TN 37996-1600, USA

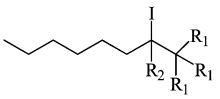
Received (in Corvallis, OR, USA) 27th February 2003, Accepted 1st May 2003
First published as an Advance Article on the web 3rd June 2003

The laser-induced photochemistry of 2-iodooctane in methanol at 266 nm occurs exclusively by homolytic reactions. This is in contrast to the lamp-induced photochemistry which is largely ionic.

Kropp has shown in extensive studies on the photochemistry of alkyl halides that radical pairs are intermediates in non-polar media.[1] Ion pairs are also formed in polar solvents, with carbenes also being formed in certain cases. We recently studied the photochemistry of racemic (**1a**) and resolved 2-iodooctane (**1b**) in the gas phase, cyclopentane, 2-methyl-2-propanol, and methanol to observe the effect of solvent polarity and viscosity on *F*, the fraction of radical pair and/or ion pair going on to products.[2] For methanol, the polar solvent of interest here, greater than half of the reaction proceeded through an ion pair and as little as one-fifth through a radical pair; $F = 0.57$ under these circumstances. We report here that, when 2-iodooctane (**1a–d**) in methanol is photolyzed with the fourth harmonic of a Nd-YAG laser at 266 nm, all of the features observed with a lamp disappear and a new photochemistry emerges. This chemistry to be described below represents an interesting way in which a one-photon photoreaction largely ionic in character is replaced by one with no ionic character under multi-photon excitation.[3]



1a: racemic
1b:*R* enantiomer



1c: $R_1 = H, R_2 = D$
1d: $R_1 = D, R_2 = H$

Photolysis of **1a**[4] in degassed methanol in a Rayonet reactor with 2537 Å lamps afforded 11 organic products (Table 1, column 2) plus HI and I_2. All of the oxygenated products (53%) arose, directly or indirectly, from the 2-octyl carbocation. Most of the octane and the two 7,8-dimethyltetradecanes (20%), on the other hand, arose from the 2-octyl radical. The three octenes may have formed from either intermediate. Based on the behavior of 2-deuterio-2-iodooctane (**1c**), approximately one third of the octane (no D) arose from the 2-octyl carbene. The 2-octyl carbocation and radical existed in part in ion and radical pairs, respectively, which not only reacted to give products but also reverted to reactant. This was evident in the photochemistry of (*R*)-2-iodooctane (**1b**) which racemized faster than it was destroyed. From this behavior the value of *F* mentioned above was determined.

Contrast the results obtained from the lamp to the photochemistry of 2-iodooctane in degassed methanol using the 4th harmonic from a pulsed (5 nsec) Nd-YAG laser (266 nm; unfocussed; 1 mJ pulse^{-1} 1.27×10^6 watts cm^{-2}). Here only the three alkenes and a trace of octane were produced (Table 1, column 3). The alkenes and 2-methoxyoctane, the major product in the lamp photochemistry, did not react when exposed to the laser light. Photolysis of **1c** yielded each alkene with one deuterium, while photolysis of **1d** afforded the two 2-octenes with three D's and 1-octene with two D's. Thus none of the products arose from the 2-octyl carbene.

By examining the extent of reaction as a function of laser power, it was possible to estimate how many photons (*n*) are responsible for the photochemistry. When the experiment was carried out in a 1 cm cell, $n = 2.4$ was obtained. A value of three photons involved in the overall chemistry is likely. Reasons why a fractional value of *n* was obtained are described in the ESI†.

The *F* value for the reaction was determined by following two things as a function of time: the disappearance of reactant and the change in optical activity of a solution of **1b** in methanol. In the 1 cm cell, the value of $F = 1$ was obtained. This is most easily seen in the data of Table 2 where the enantiomeric excess of the substrate remains close to 100% during the time in which 40% of the reactant has disappeared.

These results might be rationalized by a concerted loss of HI–DI from a super excited state of 2-iodooctane formed by three-photon excitation. This excited state, which would lie 13.9 eV above the ground state, is well above the ionization threshold of

Table 1 Photoproducts and yields (%) from the photochemistry of 2-iodooctane[a]

	Lamp	Laser		
Photochemistry	Methanol	Methanol	Gas	Cyclopentane
Octane	4	53	4	28
(*E*)-2-Octene	17	trace	10	24
Octane	10	32	6	31
(*Z*)-2-Octene	6	15	3	17
7,8-Dimethyltetradecane (isomer 1)[b]	1		13	
7,8-Dimethyltetradecane (isomer 2)[b]	2		64	trace
Unknown	7			
2-Octanol	trace			
3-Methoxyoctane	10			
2-Methoxyoctane	38			
2-Octanone	5			

[a] Reactions often contained unreacted 2-iodooctane. Products normalized to 100%. [b] *Meso* or *d,l* isomer, shown in order of elution.

---

† Electronic supplementary information (ESI) available: experimental details and methodological results on the determination of the power dependence and *F*. See http://www.rsc.org/suppdata/cc/b3/b302814n/

DOI: 10.1039/b302814n

the substrate at approximately 9 eV.[5] Data to be presented now suggest that another mechanism operates. Octane, a free-radical product, is formed in trace amounts in methanol. When the substrate in degassed cyclopentane is photolyzed with 266 nm laser light, a trace of one of the 7,8-dimethyltetradecanes is the product (Table 1, column 5). This product can only arise by the dimerization of the 2-octyl radical. This is even more manifest in the gas-phase laser-induced photoreaction where 77% of the product mixture consists of the two dimers. Since the 2-octyl radical is clearly formed in cyclopentane and the gas phase, it is reasonable to assume that it is also formed in methanol.

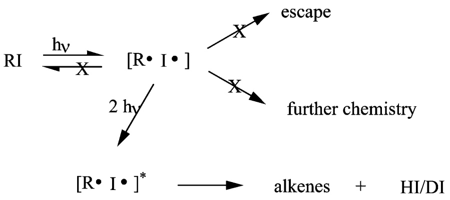
There have been numerous studies on the multiphoton photochemistry of alkyl halides, most notably CH_3I, in the gas phase.[6] Numerous resonant and non-resonant ionization and dissociation mechanisms for CH_3I have been formulated. Of significance to the chemistry described here is the mechanism involving one-photon dissociation to yield $CH_3^{\cdot}$ and $I^{\cdot}$ followed by multiphoton excitation/ionization of the radicals.[7]

The reaction thus described here commences by a one-photon excitation to produce the very short-lived $n \rightarrow \sigma^*$ excited state which dissociates into a radical pair consisting of the 2-octyl radical ($R^{\cdot}$) and iodine atom. Under the low power density lamp conditions the photochemistry is over and the remaining chemistry is dictated by the behavior of the radical pair which can reform reactant, react to given alkenes and HI, escape in the bulk solvent, and, most significantly, undergo electron transfer to yield an ion pair (R^+I^-). The cleavage of the carbon–iodine bond to form a radical pair and subsequent electron transfer take place in the picosecond time regime.[8] In the intense field of the laser pulse (width 5 ns), however, one of the components in the radical pair undergoes two-photon excitation to form a radical pair excited state before the original radical pair has the opportunity to undergo any of the chemistry noted above. Most likely, the 2-octyl radical is excited to a Rydberg state. The methyl radical, a model of the 2-octyl radical, for example, undergoes two-photon excitation to a Rydberg state at 266.7 nm in the gas phase.[9] The excited radical pair then reacts internally to yield the three alkenes and HI/DI.

Table 2 Photochemical behavior of (*R*)-2-iodooctane with 266 nm laser light in methanol

Time (min)	([*R*] + [*S*])/[R_0][a]	([*R*] − [*S*])/[R_0][b]	ee[c]
0	1	1	1
5	0.88	0.85	0.97
10	0.81	0.79	0.98
15	0.79	0.76	0.96
20	0.75	0.74	0.99
30	0.68	0.66	0.97
40	0.60	0.59	0.98

[a] Measured by gc/ms. [b] Determined by polarimetry. [c] ee = enantiomeric excess of 2-iodooctane.



If one in general could suppress the formation of an ion pair and its subsequent carbocation chemistry by diverting its radical pair precursor by its rapid excitation, this would represent a unique method for converting an ionic into a free radical reaction.

This work was supported by the National Science Foundation.

Notes and references

1 (*a*) P. J. Kropp, G. S. Poindexter, N. J. Pienta and D. C. Hamilton, *J. Am. Chem. Soc.*, 1976, **98**, 8135; (*b*) P. J. Kropp, J. A. Sawyer and J. J. Snyder, *J. Org. Chem.*, 1984, **49**, 1583; (*c*) P. J. Kropp, *Acc. Chem. Res.*, 1984, **17**, 131; (*d*) P. J. Kropp and R. L. Adkins, *J. Am. Chem. Soc.*, 1991, **103**, 2709.

2 F. Gao, D. Boyles, R. Sullivan, R. N. Compton and R. M. Pagni, *J. Org. Chem.*, 2002, **67**, 9361.

3 (*a*) J. C. Scaiano, L. J. Johnston, W. G. McGimpsey and D. Weir, *Acc. Chem. Res.*, 1988, **21**, 22; (*b*) R. M. Wilson and K. A. Schnapp, *Chem. Rev.*, 1993, **93**, 223.

4 J. San Filipo Jr and L. J. Romano, *J. Org. Chem.*, 1975, **40**, 1514.

5 Estimated from the values of iodopropanes, -butanes and -pentanes found in (*a*) R. A. Boschi and D. R. Salahab, *Mol. Phys.*, 1982, **24**, 289; (*b*) J. C. Traeger, *Org. Mass. Spec.*, 1981, **16**, 193.

6 B. Zhang, X. Wang, N. Lou, B. Zhang and J. Wei, *Spectrochim. Acta A*, 2001, **57**, 1759and references cited therein.

7 (*a*) Y. Jiang, M. R. Giorgi-Arnazzi and R. B. Bernstein, *Chem. Phys.*, 1986, **106**, 171; (*b*) S. J. Garret, D. H. Fairbrother, V. P. Holbert, E. Weitz and P. C. Stair, *Chem. Phys. Lett.*, 1994, **219**, 409.

8 (*a*) M. Lipson, A. A. Denit and K. S. Peters, *J. Phys. Chem.*, 1996, **100**, 3580; (*b*) J. Dreyer and K. S. Peters, *J. Phys. Chem.*, 1996, **100**, 15156; (*c*) M. Lipson, A. A. Deniz and K. S. Peters, *J. Am. Chem. Soc.*, 1996, **118**, 2992; (*d*) M. Lipson, A. A. Deniz and K. Peters, *Chem. Phys. Lett.*, 1998, **288**, 789.

9 J. W. Hudgens, T. G. DiGuiseppe and M. C. Lin, *J. Chem. Phys.*, 1983, **79**, 571.