

Photosolvolysis of (Iodomethyl)naphthalene. Laser Spectrophotometric Analysis of the Mechanism

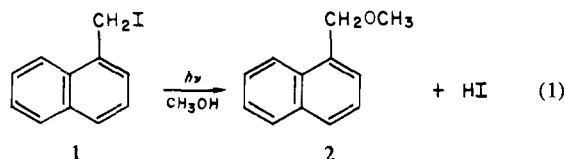
Gregory H. Slocum, Kenneth Kaufmann,[†] and Gary B. Schuster*^{†‡}

Department of Chemistry, Roger Adams Laboratory
University of Illinois, Urbana, Illinois 61801

Received April 6, 1981

Revised Manuscript Received June 4, 1981

Photosolvolysis of alkyl halides has been the theme of several recent mechanistic and synthetic studies.¹ Kropp and co-workers have investigated the photochemistry of alkyl iodides in alcohol solvents.² They observed products characteristic of both radical and carbonium ion intermediates. These findings, among others, led Kropp to propose a reaction mechanism which has as a key step electron transfer in a trappable radical pair to produce an ion pair. Similarly, recent investigations by McKenna and co-workers of the photosolvolysis of benzyl halides are interpreted in terms of the interconversion of loose singlet and triplet radical pairs, followed by electron transfer to give an ion pair.³ Also Cristol and Bindel⁴ have examined the photolysis of substituted benzyl chlorides and observed a multiplicity and substituent-dependent mixture of radical and ion derived products. We have examined the photosolvolysis of (iodomethyl)naphthalene (**1**) in methanol by using nanosecond laser spectrophotometric techniques.⁵ This investigation has revealed that the reaction product, (methoxymethyl)naphthalene (**2**), is formed as a result of a secondary reaction between photogenerated iodine atoms and iodide **1**.



Photolysis of (iodomethyl)naphthalene in oxygen-free methanol or methanol containing 20% mesitylene at room temperature with broad-band radiation from a mercury arc lamp, or at 337 nm with a nitrogen laser, gives ether **2** as the major product.⁶ There is no incorporation of deuterium in the product when this reaction is performed in CH₃OD. When oxygen is not removed from the solution 1-naphthaldehyde is also a product. In oxygen-free hexane solution the photochemistry of **1** is almost totally inhibited. These results are similar to those obtained by others for comparable systems.

[†] Fellow of the A. P. Sloan Foundation, 1977-1979.

[‡] Fellow of the A. P. Sloan Foundation, 1977-1979, and the Dreyfus Foundation, 1979-1984.

(1) Zimmerman, H. E.; Sandel, V. R. *J. Am. Chem. Soc.* **1962**, *85*, 915. Ivanov, V. B.; Ivanov, V. L.; Kuzmin, M. G. *J. Org. Chem. USSR (Engl. Transl.)* **1973**, *9*, 345. Charlton, J. L.; Williams, G. J.; Gerald, N. P. *Can. J. Chem.* **1980**, *58*, 1271. Davidson, R. S.; Goodin, J. W. *Tetrahedron Lett.* **1980**, 2911. Cristol, S. J.; Greenwald, B. E. *Ibid.* **1976**, 2105. Cristol, S. J.; Strom, R. M. *J. Am. Chem. Soc.* **1980**, *102*, 5577.

(2) Kropp, P. J.; Jones, T. H.; Poindexter, G. S. *J. Am. Chem. Soc.* **1973**, *95*, 5420. Poindexter, G. S.; Kropp, P. J. *Ibid.* **1974**, *96*, 7142. McNeely, S. A.; Kropp, P. J. *Ibid.* **1976**, *98*, 4319. Kropp, P. J.; Poindexter, G. S.; Pienta, N. J.; Hamilton, D. C. *Ibid.* **1976**, *98*, 8135. Kropp, P. J.; Gibson, J. R.; Synder, J. J.; Poindexter, G. S. *Tetrahedron Lett.* **1978**, 207. Pienta, N. J.; Kropp, P. J. *J. Am. Chem. Soc.* **1978**, *100*, 655.

(3) Appleton, D. C.; Brocklehurst, B.; McKenna, J.; McKenna, J. M.; Smith, M. J.; Taylor, P. S.; Thackeray, S.; Walley, A. R. *J. Chem. Soc., Chem. Commun.* **1977**, 108. Appleton, D. C.; Brocklehurst, B.; McKenna, J.; McKenna, J. M.; Thackeray, S.; Walley, A. R. *J. Chem. Soc., Perkin Trans. 2* **1980**, 87.

(4) Cristol, S. J.; Bindel, T. H. *J. Org. Chem.* **1980**, *45*, 951.

(5) The laser apparatus has been described: Zupancic, J. J.; Horn, K. A.; Schuster, G. B. *J. Am. Chem. Soc.* **1980**, *102*, 5279.

(6) A small amount of 1,2-dinaphthylethane (ca. 5% of the amount of **2**) is formed also. Control experiments show that the conversion of **1** to **2** is photochemical, not thermal, under the reaction conditions. The conversion is not caused by photochemical generation of a catalyst, and the quantum yields are not measurably dependent on the laser power. The products are not affected by inclusion of 20% mesitylene in the solvent (see text).

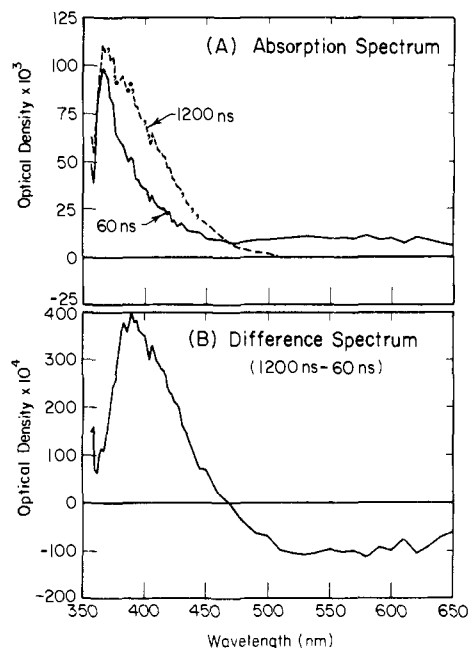


Figure 1. (A) Absorption spectra of transient products from photolysis of (iodomethyl)naphthalene (**1**) in methanol-20% mesitylene recorded 60 and 1200 ns after firing the nitrogen laser. (B) Difference spectrum between 60 and 1200 ns after the laser pulse in methanol-20% mesitylene.

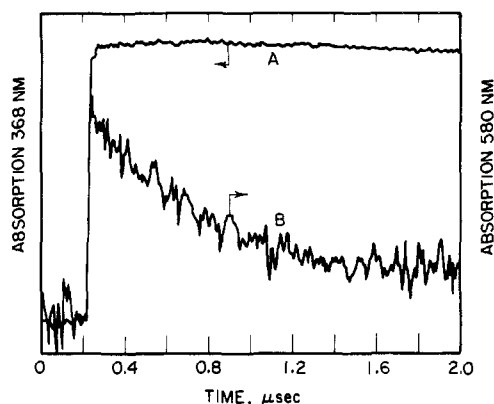


Figure 2. (A) Time dependence of absorption of naphthylmethyl radical monitored at 368 nm in methanol-20% mesitylene. (B) Time dependence of the absorption of **1**-mesitylene complex measured at 580 nm. The concentration of iodide **1** is 4.3×10^{-3} M.

Pulsed irradiation with the nitrogen laser permits spectroscopic analysis of the reactive intermediates involved in the transformation of iodide **1** to ether **2**. Figure 1a shows absorption spectra of the transient products 60 and 1200 ns after the laser pulse in oxygen-free methanol-mesitylene. A major feature of these spectra is the peak at 370 nm due to the naphthylmethyl radical (**3**),⁷ an assignment we have confirmed by independent generation of **3** from photolysis of 1-(naphthylidazo)methane in pentane.⁸ The iodine atom does not have an absorption in the spectral region we can probe. However, charge-transfer absorption of contact complexes of the iodine atom with aromatic hydrocarbons in the visible region are well-known.⁹ The transient absorption spectrum, recorded 60 ns after the pulse, exhibits a second band with a

(7) Porter, G.; Strachan, E. *Trans. Faraday Soc.* **1958**, *54*, 1595.

(8) Nakaya, T.; Tomomoto, T.; Minoru, I. *Bull. Chem. Soc. Jpn.* **1967**, *40*, 691. Zupancic, J. J.; Schuster, G. B. *J. Am. Chem. Soc.* **1980**, *102*, 5958.

(9) Strong, R. L.; Rand, S. J.; Britt, A. J. *J. Am. Chem. Soc.* **1960**, *82*, 5053. Strong, R. L. *J. Phys. Chem.* **1962**, *66*, 2423. The binding energy of these contact complexes is negligibly small; thus their formation allows spectroscopic observation of atomic iodine without much perturbation of its reactivity (Tamres, M.; Strong, R. L. In "Molecular Association"; Foster, R., Ed.; Academic Press: New York, 1979; 339-354).

Scheme I

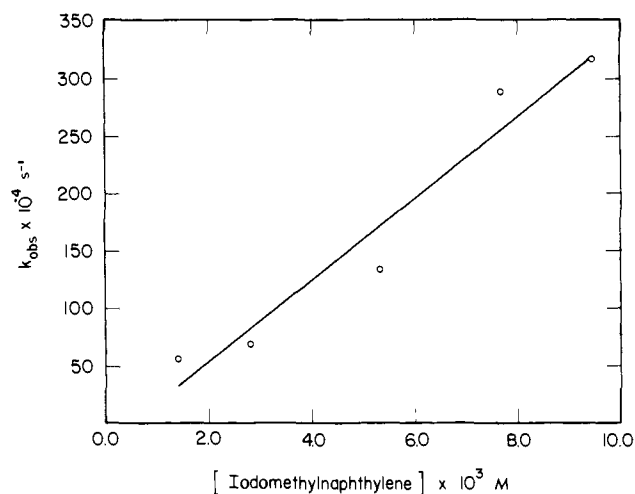
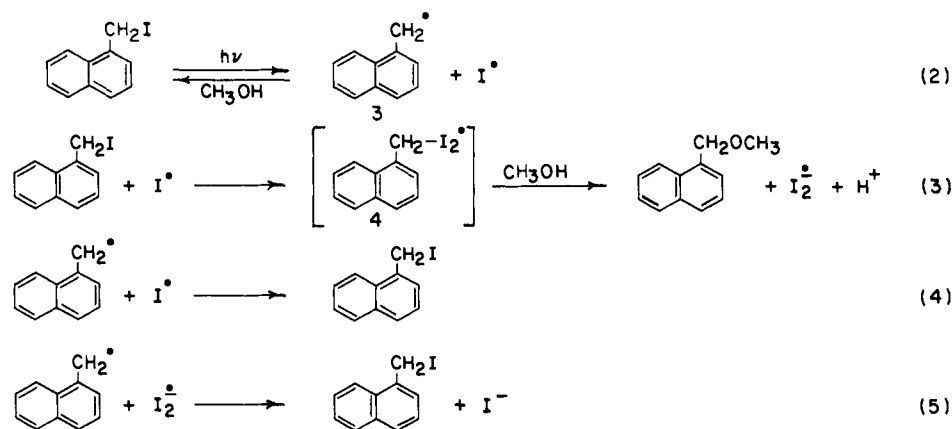


Figure 3. Rate constant for consumption of I^\bullet at increasing (iodomethyl)naphthalene **1** concentration in methanol–20% mesitylene at room temperature.

maximum at 580 nm due to the absorption of the iodine atom–mesitylene complex.⁹ Thus, this spectral evidence suggests that photolysis of **1** leads to homolytic cleavage of the carbon–iodine bond to produce naphthylmethyl radical and atomic iodine.

The laser pulse photolysis technique not only permits us to identify the transient products but also allows us to monitor time-dependent changes in the reaction mixture. The absorption spectrum recorded 1200 ns after the flash, shown in Figure 1a, reveals that the absorption due to the iodine atom complex has decayed completely and a new absorption, with a maximum at 390 nm, has grown into the spectrum. These changes are revealed more distinctly as the difference between the spectra recorded at 60 and 1200 ns shown in Figure 1b. The new absorption at 390 nm is identical with that reported for the iodine molecule radical anion (I_2^\bullet).¹⁰

If the major reaction of the iodine atom and the naphthylmethyl radical is with each other, by electron transfer or some other route, then they should be consumed at the same rate. This is not the case. Figure 2 shows the rate of decay of the absorptions due to these intermediates for a 4.3×10^{-3} M methanol–20% mesitylene solution of **1**. Quite clearly, the iodine atom reacts much faster than does the naphthylmethyl radical. The absorption of I_2^\bullet grows in as the atomic iodine is consumed. These spectral and kinetic findings indicate that the photochemically generated iodine atom reacts with some species to become eventually I_2^\bullet .

Figure 3 shows a plot of the observed rate constant for consumption of the iodine atom as the concentration of iodide **1** is increased. It is clear from these data that as the concentration

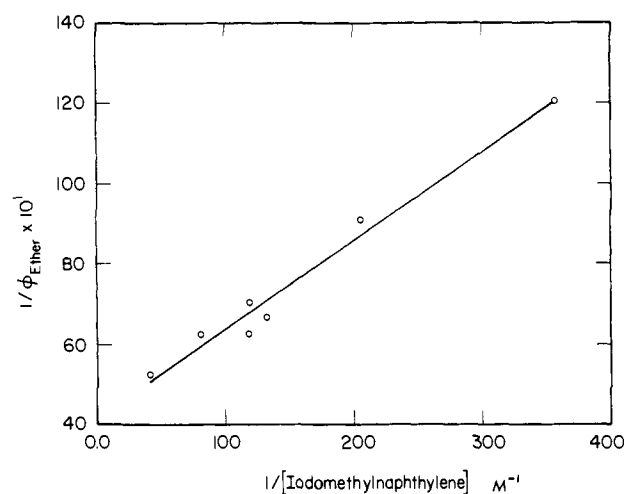


Figure 4. Double reciprocal plot of the quantum yield for ether **2** formation at increasing iodide **1** concentration in methanol at room temperature.

of **1** increases so does the rate of the reaction consuming the iodine atom. Thus the photogenerated iodine atom is reacting with iodide **1**. The rate constant for this bimolecular reaction, the slope in Figure 3, is $(3.5 \pm 0.5)10^8 \text{ M}^{-1} \text{ s}^{-1}$. Similarly, we are able to show that the rate of appearance of I_2^\bullet increases also as the concentration of **1** increases. These findings implicate a direct reaction of ground-state **1** with photochemically produced iodine atoms to generate I_2^\bullet . Analogous interactions have previously been invoked to explain the spectral properties of alkyl iodide–atomic iodine systems.¹¹ These results lead us to postulate the reaction mechanism shown in Scheme I.

The product generating step of the proposed reaction mechanism (eq 3) begins with the formation of a complex between the iodine atom and (iodomethyl)naphthalene (**1**). This step is in competition with regeneration of **1** by recombination of the naphthylmethyl radical **3** and the iodine atom (eq 4). These considerations lead to the prediction that the quantum yield of ether formation will depend upon the concentration of iodide **1**. Figure 4 is a double reciprocal plot of the quantum yield for formation of ether **2** against the concentration of **1**. Clearly, the predicted concentration dependence is verified. As the concentration of iodide **1** is increased, the quantum yield for ether formation increases also. The intercept of Figure 4 corresponds to a quantum yield for ether formation at infinite **1** concentration of 0.24. This indicates that there is extensive geminate recombination to reform **1** from the initial radical pair (eq 2).

Similarly, the mechanism shown in Scheme I leads to the prediction that inclusion of oxygen should divert naphthylmethyl

(10) DeViolet, P. N.; Bonneau, R.; Jousset-Dubien, J. *Mol. Photochem.* **1973**, *5*, 61.

(11) Brühlmann, U.; Buchler, H.; Marchetti, F.; Bühler, R. E. *Chem. Phys. Lett.* **1973**, *21*, 412. Strong, R. L.; Venditti, F., Jr. *Ibid.* **1977**, *46*, 546.

radical (3) to, eventually, naphthaldehyde without affecting any of the reactions that form ether 2 (O₂ does not react rapidly with I⁻). This prediction also is verified by experiment. The quantum yield of ether formation is essentially unaffected by the addition of oxygen to the reaction mixture; however, the quantum yield for total disappearance of iodide 1 more than doubles when oxygen is present.

The last step in the proposed mechanism is the reaction of the naphthylmethyl radical with I₂⁻ to regenerate 1 and form iodide ion. The evidence for this step is that the rates of consumption of the radical and I₂⁻, in the absence of oxygen, are approximately the same.

In sum, our kinetic, spectroscopic, and product studies implicate a secondary reaction of iodine atoms with alkyl iodide 1 as the product generating step in this photosolvolysis reaction. The complex formed in this step may rapidly dissociate into separated ions or may react directly with solvent. There is no evidence in this system for the direct photochemical generation of carbonium ions or for their formation by electron transfer from the naphthylmethyl radical to iodine atoms. However, it must be noted that the mechanism for photosolvolysis of these halides may depend strongly upon the identity of the halogen atom and the structure of the alkyl group. We are continuing to explore the photosolvolysis mechanism of iodide 1 and its relationship to the other systems that have been reported.

Acknowledgment. We thank Professor Robert L. Strong of Rensselaer Polytechnic Institute for some very helpful suggestions and comments, John Hurst of this department for the use of his computer programs, and James Wehmer of this department for his assistance with the laser apparatus. This work was supported by the National Science Foundation and the donors of the Petroleum Research Fund, administered by the American Chemical Society.

Catalysis by Solvated Transition-Metal Cations. Novel Catalytic Transformations of Alkenes by Tetrakis(acetonitrile)palladium Ditetrafluoroborate. Evidence for the Formation of Incipient Carbonium Ions as Intermediates

Ayusman Sen* and Ta-Wang Lai

Chandlee Laboratory, Department of Chemistry
The Pennsylvania State University
University Park, Pennsylvania 16802

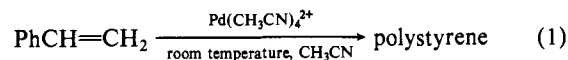
Received December 15, 1980

An important requirement of homogeneous catalysts is that they have the ability to create vacant coordination sites by dissociation of weakly held ligands. Transition-metal cations solvated in weakly coordinating solvents and having noncoordinating counteranions would be expected to meet this criterion. Furthermore, the catalytic properties of such compounds should be subject to modification in a predictable way by the stepwise substitution of solvent molecules by other more strongly binding ligands. In this context, we report the catalytic properties of [Pd(CH₃CN)₄](BF₄)₂ (1) and its trisphosphine derivative [Pd(CH₃CN)(PPh₃)₃](BF₄)₂ (2). As detailed below, the chemistry associated with 1 was found to differ very significantly from that observed with analogous neutral Pd(II) compounds, such as Pd(PhCN)₂Cl₂, PdCl₂, and Pd(OAc)₂, as well as other conventional, neutral transition-metal compounds on one hand and traditional Lewis acids such as AlCl₃ on the other.

Compound 1 was synthesized through the interaction of palladium metal with 2 equiv of nitrosyl tetrafluoroborate in acetonitrile.¹ Following precipitation by the addition of methylene chloride, an air-sensitive yellow solid was isolated.² Addition of

an excess of PPh₃ to 1, suspended in methylene chloride, resulted in the quantitative formation of 2, isolated as air-stable, pale greenish yellow solid.³

Dropwise addition of styrene to an acetonitrile solution of 1 resulted in the immediate and quantitative precipitation of polystyrene (eq 1). When a monomer to catalyst ratio of 100:1



was used, a polymer of average molecular weight ~70 000 was obtained.⁴ Catalytic polymerization of styrene has not been observed with neutral Pd(II) compounds;⁵ 2 was also found to be inactive under identical conditions. Significantly, another electrophilic cation, Ag⁺, also catalyzes polymerization of styrene,⁶ although at an appreciably higher temperature (70 °C vs. room temperature for 1).

Compound 1 also catalyzed the oligomerization of unactivated olefins such as ethylene. In a typical reaction, a solution containing 0.1 mmol of 1 in 0.3 mL of CH₃CN was exposed to ethylene (at 1200 psi) at 40 °C for 60 h. At the end of this period, a colorless organic layer (~0.9 mL) was found to have been formed over the original acetonitrile layer.⁷ Analysis⁸ of this layer revealed it to be an approximately equal mixture of C₄-, C₆-, C₈- as well as a small amount of C₁₀-internal monoolefins, the overall reaction representing a "turnover" of 200 equiv (relative to 1) of ethylene (eq 2). The formation of internal olefins is not surprising since



1 in acetonitrile solution or chloroform suspension was found to convert both 1-butene and *cis*-2-butene to the thermodynamic equilibrium mixture of *trans*-2-butene, *cis*-2-butene, and 1-butene (observed percentages are 67%, 28% and 5%, respectively),⁹ within 1 h at room temperature. In addition, this equilibrium mixture was converted to butene dimers in <2 days. The catalytic formation of C₈-monoolefins from butenes indicate that the oligomerization of ethylene by 1 may proceed through discrete dimerization steps. Significantly, unlike most ethylene oligomerization catalysts,¹¹ the oligomerization of ethylene by 1 does not stop at the dimer stage. This may be due to the fact that while neutral, electron-rich transition-metal centers bind ethylene more strongly than butenes,¹² in the case of electrophilic Pd(CH₃CN)₄²⁺, with minimal steric requirements, the bulky electron-rich butenes may be able to compete effectively with ethylene in the dimerization process. As an extension of the above argument, one would predict that substitution of some of the CH₃CN molecules in 1 by other bulkier, more electron-donating ligands would favor the formation of C₄- over C₆- and C₈-monoolefins, and indeed in

(2) Anal. Calcd for [Pd(CH₃CN)₄](BF₄)₂: C, 21.7; H, 2.7; N, 12.6. Found: C, 21.8; H, 2.9; N, 12.3. IR (Nujol) $\nu(\text{C}=\text{N})$ 2335 cm⁻¹; $\nu(\text{BF}_4^-)$ 1100-1000, 760 cm⁻¹.

(3) ³¹P NMR (CDCl₃, -40 °C) δ P₁ 34.5 (1 P, t), δ P₂ 27.6 (2 P, d); IR (nujol) $\nu(\text{C}=\text{N})$ 2375, 2335 cm⁻¹; $\nu(\text{BF}_4^-)$ 1100-1000, 760 cm⁻¹.

(4) Molecular weights of polymers determined by gel permeation chromatography using standard polystyrene samples as calibrants.

(5) P. M. Maitlis, "The Organic Chemistry of Palladium", Vol. II, Academic Press, New York, 1971, Chapter I.

(6) (a) M. M. T. Khan and A. E. Martell, "Homogeneous Catalysis by Metal Complexes", Vol. II, Academic Press, New York, 1974, Chapter 6. (b) J. P. Hermans and G. Smets, *J. Polym. Sci., Part A*, 3, 3175 (1965).

(7) A trace of palladium metal was sometimes observed following deprotonation. This was found to be inactive in a separate experiment.

(8) Hydrocarbon samples were analyzed by standard gas chromatography-mass spectrometric techniques.

(9) Typical reported percentages were 69%, 25%, and 6%, respectively.¹⁰

(10) (a) M. Tuner, J. v. Jouanne, H.-D. Brauer, and H. Kelm, *J. Mol. Catal.*, 5, 425, 433, 477 (1979); (b) C. A. Tolman, *J. Am. Chem. Soc.*, 94, 2994 (1972).

(11) G. Lefebvre and Y. Chauvin, *Aspects Homogeneous Catal.*, 1, 107 (1970).

(12) (a) F. R. Hartley, *Chem. Rev.*, 73, 163 (1973); (b) C. A. Tolman, *J. Am. Chem. Soc.*, 96, 2780 (1974).

(1) R. F. Schramm and B. B. Wayland, *Chem. Commun.*, 898 (1968).