integrations of the Oregonator. We assume that the relaxation amplitudes of the model are too small to be observed in comparison to the amplitude of the damped oscillator. Furthermore, the Oregonator model does not include the complex organic chemistry involved in malonic acid oxidation. The relationship of the damping constant with other kinetic variables such as concentrations and k_f values is extremely complex for the Oregonator model and may not be given by a simple closed-form expression.

Entrainment of the BZ reaction was measured experimentally[6] and calculated under conditions for which the Oregonator shows limit cycle oscillations (in the *absence* of external Br^-). Since the free-running BZ oscillations are nonsinusoidal and complex, there appears to be some ambiguity in the quantitative interpretation of entrainment in this case.

Further work on the influence of forcing amplitude, flow rate, concentrations, and temperature is in progress.

Acknowledgment. We thank the Fonds der Chemischen Industrie for partial support of this work.

---

(6) Thönnissen, H., Zulassungsarbeit, University of Würzburg, 1983.

Reaction of Fluorine Atoms with Alkyl Iodides: A Possible Observation of the Walden Inversion in the Gas Phase

T. V. Venkitachalam, P. Das, and R. Bersohn*

Department of Chemistry, Columbia University
New York, New York 10027

Received May 23, 1983

When fluorine atoms attack methyl iodide molecules, three reactions are possible:

$$F + CH_3I \xrightarrow{1} CH_3 + IF \qquad \Delta D_0° = -10.3 \text{kcal/mol}^1 \qquad (1)$$

$$F + CH_3I \xrightarrow{2} CH_2I + HF \qquad \Delta D_0° = -36.5 \text{ kcal/mol} \qquad (2)$$

$$F + CH_3I \xrightarrow{3} CH_3F + I \qquad \Delta D_0° = -70.9 \text{kcal/mol} \qquad (3)$$

Reaction 1 has been studied by crossed molecular beams[2] and by laser-induced fluorescence of the IF product.[3] In this communication we show that reaction 3 does occur and present some evidence that the Walden inversion takes place in the gas phase. This system of reactions has been studied by mass spectrometric analysis of a flowing reaction system.[4] The overall rate constant $k = k_1 + k_2 + k_3$ is 2×10^{-10} cm^3/(molecule s), and k_3 was estimated to be $<0.3k$. Studies with ^{18}F atoms have shown that the rate constant for reaction 3 is $8 \pm 3 \times 10^{-13}$ cm^3/molecules·s.[9]

A two-photon laser-induced fluorescence technique[5] has been recently developed for detecting iodine atoms in either the $^2P_{3/2}(I)$ or the $^2P_{1/2}(I^*)$ state. In this method two photons are absorbed at 304.7 and 306.7 nm by the I and I* atoms, respectively. The excited iodine atoms emit an infrared photon followed by a vacuum ultraviolet photon, which is detected.

In our experiments SF_6 and an alkyl iodide at equal pressures were mixed and flowed through a reaction vessel at a total pressure of 0.2 torr. A CO_2 laser pulse (0.5-μs duration, 10.6 μm, 0.5 J/pulse) dissociated the SF_6 to F and SF_5. One microsecond later a dye laser was fired. At these low pressures and short times single collisions predominate. The experiment was repeated at 5 Hz while the dye laser was gradually swept through the I and I* absorption peaks at 304.7 and 306.7 nm. The resulting fluorescence intensities for the I and I* atoms are shown in Figure 1 for methyl, ethyl, isopropyl, and *tert*-butyl iodide. From the relative intensities one sees that a tertiary iodide does not give iodine atoms, a secondary iodide does give some, and a primary iodide gives much more. An exactly parallel behavior is shown by the Walden inversion in solution. The ratio I*/I is 0.42 ± 0.14 for CH_3I, 0.32 ± 0.13 for C_2H_5I, and 0 for i-C_3H_7I.

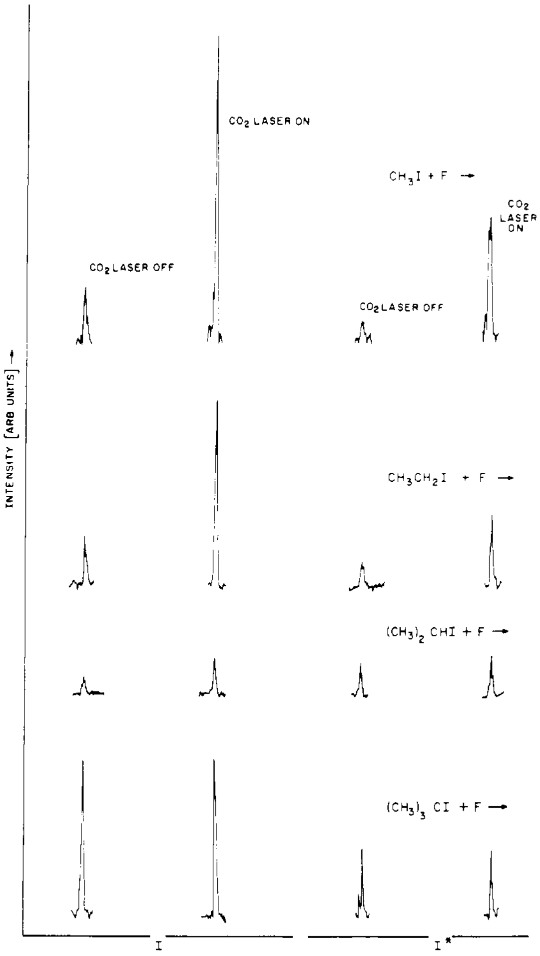

Figure 1.

Tests were made to show that the iodine atoms were not photodissociated from the alkyl iodide by the CO_2 laser or by two-photon dissociation by the dye laser of the radical product of reaction 2 or of the IF product of reaction 1. In the absence of SF_6, CO_2 laser pulses did not produce additional iodine atoms. Moreover when the delay time between the CO_2 and dye-laser pulses was lengthened from 0.5 to 1.0 μs the iodine atom signal increased showing that iodine atoms are generated by collisions. Besides the iodine atoms produced by reactive collisions, iodine atoms are also produced during the probing pulse by a two-photon absorption by the alkyl iodide. The contribution that these latter iodine atoms make to the observed iodine fluorescence signal is a result of two successive two-photon absorptions. The dye-laser power is adjusted so that the iodine atom fluorescence with the CO_2 laser on is maximized relative to that with the CO_2 laser off. The radical products such as CH_2I are much less abundant than the parent and presumably have similar absorption coefficients at the probing wavelengths. As for IF, strong laser-induced fluorescence signals were seen for it from the alkyl iodides discussed here and also CF_3I but iodine atom signals were not seen for t-BuI and CF_3I. Experiments at 100 mtorr of CH_3I and SF_6 pressures varying between 25 and 125 mtorr showed that the I atom fluorescence intensities varied linearly with the SF_6 pressure

---

(1) Thermochemical data are from: Okake, H. "Photochemistry of Small Molecules"; Wiley: New York, 1978.

(2) Farrar, J. M.; Lee, Y. T. *J. Chem. Phys.* **1975**, *63*, 3639.

(3) Stein, L., Wanner, J.; Walther, H. *J. Chem. Phys.* **1980**, *72*, 1128.

(4) Leipunskii, I. O.; Morozov, I. I.; Tal'Roze, V. L. Dokl. Chem. (*Engl. Transl.*) **1971**, *198*, 1367.

(5) Brewer, P.; Das, P.; Ondrey, G.; Bersohn, R. *J. Chem. Phys.* **1983**, *79*, 720.

(6) Brooks, P. R.; Jones, E. M. *J. Chem. Phys.* **1966**, *45*, 3449.

(7) Parker, D. H.; Chakravorty, K. K.; Bernstein, R. B. *Chem. Phys. Lett.* **1982**, *86*, 113.

0002-7863/83/1505-7452$01.50/0

thus ruling out any appreciable generation of I atoms by F atom attack on products of reactions 2 and 3, i.e., CH_2I and IF.

Reaction 3 is an extremely exothermic reaction. It is therefore reasonable to assume that some of the decline in the potential energy takes place already in the entrance channel; in other words the fluorine atom is attracted to the back side of the CH_3I molecule just as it is to the front. Supporting this assumption is the fact that when excess argon was added to the reaction mixture to thermalize the fluorine atoms, no effect was seen on the I atom yield. (The F atoms photodissociated from SF_6 move relatively slowly but an appreciable fraction have kinetic energies of 2-4 kcal/mol.[8]) However, when sufficiently bulky groups are present the fluorine atom cannot approach closely enough to the carbon atom to feel its attraction, and there is a barrier in the entrance channel.

How can one prove that the reaction producing iodine atoms is truly a Walden inversion, i.e., that the F atom approaches from the backside of the carbon atom? A classical proof would begin with an optically active iodide and show that the product fluoride had the opposite configuration. A direct proof would be to carry out the reaction with beams of F atoms and oriented CH_3I molecules[6,7] and to show that the reaction cross section increased when the CH_3 group was oriented toward the F atom beam. Here we rely on a less rigorous argument. The reaction does not take place with an alkyl iodide such as *tert*-butyl iodide that is strongly hindered on its backside. Neither does it take place with CF_3I. On the other hand the IF-producing reaction appears to take place with all alkyl iodides. Thus we conclude that reactive attack of the F atom on the I atom side of the molecule always produces IF and does not result in displacement of an I atom. Attack from the rear dislodges an I atom only when the steric hindrance is not too great.

Acknowledgment. This work was supported by the U.S. Department of Energy. We are grateful to T. Allik for generous help in setting up the CO_2 laser.

Registry No. CH_3I, 74-88-4; CH_3CH_2I, 75-03-6; $(CH_3)_2CHI$, 75-30-9; $(CH_3)_3CI$, 558-17-8; CF_3I, 2314-97-8; F, 14762-94-8.

---

(8) Grant, E. R.; Coggiola, M. J.; Lee, Y. T.; Schultz, P. A.; Sudbo, A. S.; Shen, Y. R. In "State-to-State Chemistry"; Brooks, P. R., Hayes, E. J., Eds.; American Chemical Society: Washington, DC, 1977; p 72.

(9) Iyer, R. S.; Rowland, F. S. *J. Phys. Chem.* **1981**, *85*, 2488.

Oxidation of NADH by Ferrocenium Salts. Rate-Limiting One-Electron Transfer

Brian W. Carlson and Larry L. Miller*

Department of Chemistry, University of Minnesota
Minneapolis, Minnesota 55455

Received July 5, 1983

Because the coenzyme couples $NADH/NAD^+$ and $NADPH/NADP^+$ are ubiquitous and control so much of our oxidation, reduction nature, there has been a long standing interest in the mechanisms of the redox interconversions. Chemists have given considerable attention to oxidations of NADH and its analogues in enzyme-free systems[1] and the questions recently have become sharply focused on single-step hydride transfer vs. multistep processes involving initial electron transfer from NADH to the oxidant. Of particular interest have been studies that reported isotope effects[2] or correlations of thermodynamic and kinetic data.[3]

Scheme I

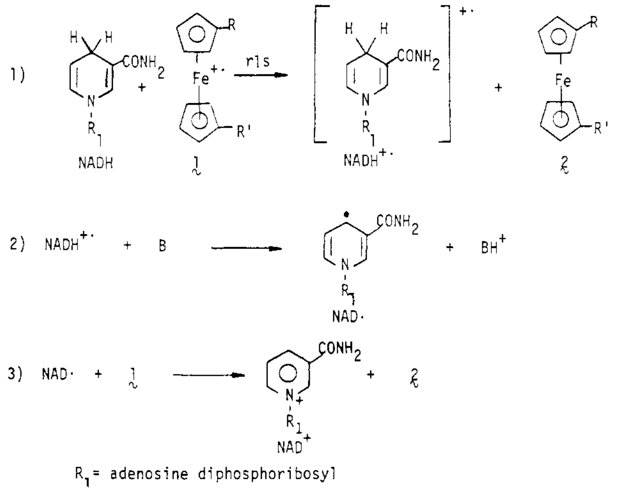

Table I. Oxidation of NADH by **1a**[a]

[NaClO$_4$]	$k/(M^{-1}\ s^{-1})$ ± std deviation	no. of runs
0.1	5.41 ± 0.26	17
0.2	3.29 ± 0.13	15
0.3	2.40 ± 0.11	14
0.4	1.90 ± 0.05	8
0.5	1.55 ± 0.08	12

[a] Conditions cited in text.

Table II. Oxidation of NADH by Ferrocenium Ions **1**[a]

R, R' (in 1)	$k_0/(M^{-1}\ s^{-1})$	K^b
H, H	13.7	15.6
HgCl, H	16.3	15.9
n-Bu, H	4.55	12.2
Et, H	2.99	9.2
CH_3, CH_3	0.629	7.6

[a] k_0 = extrapolated rate constant at zero [NaClO$_4$]. [b] K = apparent ion pair equilibrium constant obtained from slope of k_{-1} vs. [NaClO$_4$] plot.

In the present investigation we set out to study an NADH oxidation that could be demonstrated, as unequivocally as possible, to involve initial one-electron transfer from NADH to the oxidant. In this communication we document the experiments and report on some of the broader implications of the results. In particular, the data provide an estimate of the $E^{\circ\prime}$ for the *one-electron, no proton* $NADH/NADH^{+\bullet}$ couple. This value cannot be determined directly because of the instability of $NADH^{+\bullet}$,[4] and uncertainty remains in the literature about the energetics of $NADH/NADH^{+\bullet}/NAD\bullet$ interconversions.[5]

Kinetic experiments were performed using β-NADH and a series of substituted ferrocenium hexafluorophosphates.[6] Reaction products and the stoichiometry of the reaction of **1a** (R, R' = H) and NADH in buffered aqueous propanol[7] were demonstrated by reacting a 2/1 molar ratio of **1a**/NADH. The two reactants were completely consumed and NAD^+ and ferrocene (**2a**) were isolated, each in >75% yield. Typical kinetic experiments involved

---

(1) (a) Creighton, D. J.; Hajdu, J.; Sigman, D. S. "Bioorganic Chemistry"; Academic Press: New York, 1978; Vol. IV, Chapter 14. (b) Kill, R. J.; Widdowson, D. A. "Biorganic Chemistry"; Academic Press: New York, 1978; Vol. IV, Chapter 8.

(2) (a) Steffans, J. J.; Chipman, D. M. *J. Am. Chem. Soc.* **1971**, *93*, 6694. (b) Chipman, D. M.; Yaniv, R.; van Eikeren, P. *Ibid.* **1980**, *102*, 3244. (c) Creighton, D. J.; Hajdu, J.; Mooser, G.; Sigman, D. S. *Ibid.* **1973**, *95*, 6855. (d) Ohno, A.; Yamamoto, H.; Oka, S. *Ibid.* **1981**, *103*, 2041. (e) Ohno, A.; Shio, T.; Yamamoto, H.; Oka, S. *Ibid.* **1981**, *103*, 2045. (f) Kurz, L. C.; Frieden, C. *Ibid.* **1980**, *102*, 4198.

(3) (a) Powell, M. F.; Bruice, T. C. *J. Am. Chem. Soc.* **1982**, *104*, 5834. (b) Roberts, R. M. G., Ostovic, D.; Kreevoy, M. M. *Faraday Discuss. Chem. Soc.* **1982**, *74*, 257.

(4) Grodkowski, J.; Neta, P.; Carlson, B. W.; Miller, L. L. *J. Phys. Chem.* **1983**, *87*, 3135.

(5) See, for example: Powell, M. F.; Bruice, T. C. *J. Am. Chem. Soc.* **1983**, *105*, 1014.

(6) Duggan, D. M.; Hendrickson, D. N. *Inorg. Chem.* **1975**, *14*, 955.

(7) The solvent was 46/54 1-PrOH/H_2O (w/w) with the aqueous portion being 0.02 M in pH 7.0 phosphate buffer. Values cited for pH refer to the aqueous solutions before mixing. All reactions were conducted at 30.0 ± 0.2 °C under an atmosphere of argon. Various concentrations of NaClO$_4$ were added.

0002-7863/83/1505-7453$01.50/0