toward S(1) (intramolecular distance 2.91 Å). Although the bond length S(4)-S(5) (2.101 Å) is somewhat shorter than that of S(1)-S(2) (2.149 Å) (Table I), both values are about 0.1 Å longer than expected for disulfur ligands,[7] in agreement with the low-frequency IR bands at 495 and 445 cm^{-1}, although another IR absorption is observed at 598 cm^{-1}.

Considering the new ligand $\eta^1(\mu\text{-S,S})$ as a two-electron donor similar to the ligand μ-S and the ligand $\eta^2(\mu\text{-S},\mu\text{-S})$ as a six-electron donor, the Cr atoms achieve noble gas configuration provided a metal-metal double bond is assumed. Alternatively, taking the C_5Me_5 ligands as monoanions and the three different sulfur ligands as dianions, each of the Cr atoms is left in a d^2 configuration and a Cr-Cr double bond is required to explain the diamagnetism of the complex. In agreement with these considerations a Cr-Cr distance of 2.489 Å is found, which is slightly longer than in the starting material (2.28 Å).[8]

At the moment it is not clear why the coordination of a $\eta^1(\mu\text{-S,S})$ disulfur ligand is preferred to a simple μ-S ligand, which is electronically equivalent. In any case no compound of the composition $(C_5Me_5)_2Cr_2S_4$ has been observed in the reaction of $[(C_5Me_5)_2(CO)_2Cr]_2$ with sulfur, but it is formed by sulfur abstraction from $(C_5Me_5)_2Cr_2S_5$ with $P(C_6H_5)_3$.[9] However, extended studies on the reaction of $(C_5Me_5)_2M_2(CO)_4$ (M = Mo, W) with S_8 show that in the molybdenum and tungsten series under the same conditions several isomers of composition $(C_5Me_5)_2M_2S_4$ can be obtained.[10]

Acknowledgment. We thank the Deutsche Forschungsgemeinschaft, the Fonds der Chemischen Industrie, and the BASF AG for support of this work.

Registry No. $(C_5Me_5)_2Cr_2S_5$, 80765-35-1; $[(\eta^5\text{-}C_5Me_5)(CO)_2Cr]_2$, 37299-12-0; S_8, 10544-50-0.

Supplementary Material Available: A listing of atomic positions and thermal parameters (2 pages). Ordering information is given on any current masthead page.

---

[8] Potenza, J.; Giordano, P.; Mastropaolo, D.; Efraty, A. *Inorg. Chem.* **1974**, *13*, 2450.

[9] Unpublished results.

[10] Brunner, H.; Guggolz, E.; Meier, W.; Wachter, J.; Ziegler, M. L., to be submitted for publication.

Effect of Reagent Rotation on Cross Section for the Reaction Li + FH → LiF + H

I. NoorBatcha[1a,b] and N. Sathyamurthy*[1c,d]

Department of Chemistry
Indian Institute of Technology
Kanpur 208016, India

Received September 9, 1981

In this communication, we report on the effect of reagent rotation on the cross section for the reaction

$$\text{Li} + \text{FH} \rightarrow \text{LiF} + \text{H} \qquad (1)$$

for HF in its $v = 2$ vibrational state in the range of rotational state $0 \leq J \leq 9$, at a relative translational energy of $T = 8.7$ kcal mol^{-1}, based on three-dimensional quasi-classical trajectory[2] (QCT) studies on an ab initio potential-energy surface (PES).[3,4] The reaction cross section (S_r) decreases initially and then increases with an increase in J. The former effect is attributed to the disruption of the favored orientation for the reaction. The latter effect is explained on the basis of the F-H bond stretching due to centrifugal distortion at large (J, v). Under the conditions employed in this study, at large J, *reagent rotation is nearly 4 times more efficient than reagent vibration*, which in turn is more effective than reagent translation in causing the reaction.

Although the last 20 years have witnessed an increase in understanding of the effect of reagent translation and vibration[5] on the rates of chemical reactions, the study of the effect of reagent rotation has been limited, and as a result, the understanding of the role of reagent rotation in chemical reactions has remained poor.

The QCT studies[6] of the effect of J on S_r have mostly focused their attention on the reaction

$$\text{F} + \text{H}_2 \rightarrow \text{FH} + \text{H} \qquad (2)$$

and its isotopic analogues. Depending on the PES employed, the effect of increasing J on S_r was varied: (1) a dramatic drop in S_r followed by a leveling off of the same; (2) a slight increase in S_r from $J = 0$ to 1 followed by a decrease in S_r; (3) a substantial initial decrease followed by an increase in S_r. Experimentally, Klein and Persky[7] showed that the rate of reaction 2 was nearly insensitive to J in the range $J = 0$–2. Bernstein[8] and co-workers showed that a small increase in the reagent rotational energy (R) resulted in a small increase in the reactivity for the reaction

$$\text{K} + \text{FCs} \rightarrow [\text{KFCs}] \rightarrow \text{KF} + \text{Cs} \qquad (3)$$

and a small decrease for the reaction

$$\text{K} + \text{FRb} \rightarrow [\text{KFRb}] \rightarrow \text{KF} + \text{Rb} \qquad (4)$$

In both cases, the effect of reagent rotation on S_r was analogous to that of relative translation.

In recent years, there have been some experimental results available for some alkali atom-hydrogen halide reactions. Blackwell et al.[9] concluded from chemiluminescence depletion experiments on the reactions

$$\text{Na} + \text{XH}\ (\text{X} = \text{F, Cl}) \rightarrow \text{NaX} + \text{H} \qquad (5)$$

that there was an initial decrease followed by an increase in the reaction rate with increase in J. The initial decline was also observed by Dispert et al.[10] for the related reaction

$$\text{K} + \text{ClH} \rightarrow \text{KCl} + \text{H} \qquad (6)$$

None of these reactions has been studied so far theoretically to understand why there is a decreasing/increasing effect of J on the reaction rate. Recently, however, for the simplest alkali atom-hydrogen halide reaction (1), a fairly accurate ab initio PES has become available[3,11] and has also been fitted to an analytic function.[4] Therefore we found this to be an ideal system for which the effect of reagent rotation on reaction cross section could be studied theoretically.

We have carried out QCT calculations for this reaction on an ab initio surface. We have chosen $v = 2$ since the chemiluminescence depletion experiments[9] on Na + FH had v in the range 1-6. The value of $T = 8.7$ kcal mol^{-1} employed in this study is the same as that employed in the only molecular-beam study[12] of this reaction (1). The details of the QCT method are described elsewhere.[2] We mention only that the impact parameter was sampled in a stratified manner and other variables of orientation angles and vibrational phase were selected randomly.

---

[1] (a) In partial fulfillment of the requirements for the degree of Doctor of Philosophy. (b) On leave from the American College, Madurai 625 010, India, under the FIP scheme. (c) This research was supported in part by a grant from the Department of Science and Technology, India. (d) The calculations reported in this paper were carried out on a DEC-1090 computer at the Indian Institute of Technology, Kanpur.

[2] Porter, R. N.; Raff, L. M. In "Dynamics of Molecular Collisions"; part B; Miller, W. H., Ed.; Plenum Press: New York, 1976; Chapter 1.

[3] Chen, M. M. L.; Schaefer, H. F., III *J. Chem. Phys.* **1980**, *72*, 4376.

[4] Carter, S.; Murrell, J. N. *Mol. Phys.* **1980**, *41*, 567.

[5] Kneba, M.; Wolfrum, J. *Annu. Rev. Phys. Chem.* **1980**, *31*, 47.

[6] Polanyi, J. C.; Schreiber, J. L. *Faraday Discuss. Chem. Soc.* **1977**, *62*, 267 and references therein.

[7] Klein, F. S.; Persky, A. *J. Chem. Phys.* **1974**, *61*, 2472.

[8] Stolte, S.; Proctor, A. E.; Pope, W. M.; Bernstein, R. B. *J. Chem. Phys.* **1977**, *64*, 3468. Zandee, L.; Bernstein, R. B. *J. Chem. Phys.* **1978**, *68*, 3760.

[9] Blackwell, B. A.; Polanyi, J. C.; Sloan, J. J. *Chem. Phys.* **1978**, *30*, 299.

[10] Dispert, H. H.; Geis, M. W.; Brooks, P. R. *J. Chem. Phys.* **1979**, *70*, 5317.

[11] Balint-Kurti, G. G.; Yardley, R. N. *Faraday Discuss. Chem. Soc.* **1977**, *62*, 77.

[12] Becker, C. H.; Casavecchia, P.; Tiedemann, P. W.; Valentini, J. J.; Lee, Y. T. *J. Chem. Phys.* **1980**, *73*, 2833.

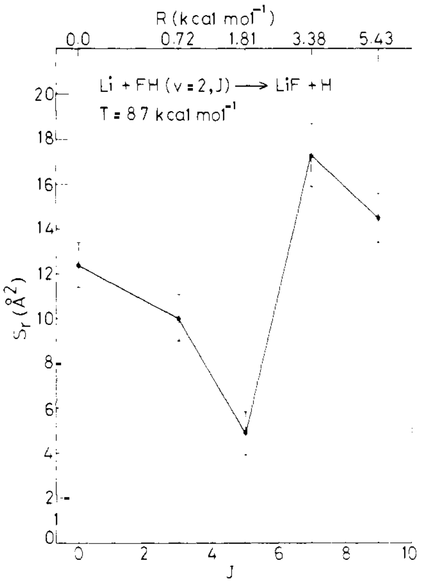


Figure 1. Reaction cross section S_r as a function of the rotational state J (lower scale) for HF ($v = 2$) at $T = 8.7$ kcal mol^{-1}. The corresponding rotational energies (in kcal mol^{-1}) are shown in the upper scale. The error bars correspond to a 95% confidence level.

The results of the QCT study are plotted in the form of S_r as a function of J in Figure 1. With increase in J from 0 to 5, there is a monotonic decrease in S_r; further increase in J to 7 and 9 results in a dramatic increase in S_r.

For reaction 1, ab initio studies[3] show that an angular approach of Li to FH at an LiFH angle of 74° has the lowest barrier, ~10 kcal mol^{-1}, for the reaction. Also, detailed analysis of the initial conditions of the reactive trajectories shows that there is a preferred cone of reaction at the F end of the HF molecule. Therefore it is understandable that an increase in J from 0 to 3-5 disrupts the preferred orientation of the reaction, resulting in a drop in the magnitude of S_r. In the absence of any additional effect, we would have expected a leveling off of S_r. However, in this particular case, because of the large vibrational energy present in the molecule, increase in J results in substantial centrifugal distortion. This means a stretching of the FH bond under attack, and the result would be similar to increasing the vibrational energy. For example, when v is changed from 0 to 1 to 2, S_r increases from 0.8 ± 0.2 to 8.7 ± 0.9 to 12.4 ± 1.0 Å^2 at $T = 8.7$ kcal mol^{-1} for $J = 0$. This is explained on the basis of the *sudden* character of the PES.[3,11,13] It must be added that such an explanation for the observed dependence of S_r on J was suggested earlier by Blackwell et al.[9] although no dynamical results were available at that time.

At large J, even though the effect of reagent rotation on S_r is qualitatively similar to that of reagent vibration, there is a quantitative difference between the two. In the energy range we have studied, $\Delta S_r/\Delta V = 0.5$ Å^2/(kcal mol^{-1}) and $\Delta S_r/\Delta R = 2.7$ Å^2/(kcal mol^{-1}); that is, rotation is nearly 4 times more efficient than vibration in enhancing the reaction cross section. Reagent translation is the least effective in this case with a $\Delta S_r/\Delta T$ value of 0.086 Å^2/(kcal mol^{-1}).

In summary our findings are significant for these reasons: (1) Ours is the first dynamical study of the effect of reagent rotation for a prototype alkali atom-hydrogen halide reaction, on an ab initio PES. (2) Increase in J results in a substantial decrease followed by a rapid increase in S_r, with a minimum occurring around $J = 5$. The results are in qualitative accord with the experimental results on the related alkali atom-hydrogen halide exchange reactions. (3) For the first time we have shown that reagent rotation can be more effective than reagent vibration in enhancing a reaction.

Registry No. Li, 7439-93-2; FH, 7664-39-3.

---

(13) Polanyi, J. C.; Sathyamurthy, *N. Chem. Phys.* **1978**, *33*, 287. NoorBatcha, I.; Sathyamurthy, N. *J. Chem. Phys.*, in press.

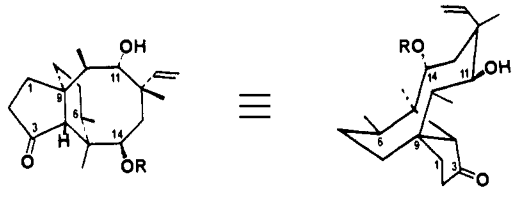
Total Synthesis of (±)-Pleuromutilin[1]

E. Grant Gibbons*

Department of Chemistry, Harvard University
Cambridge, Massachusetts 02138

Received December 7, 1981

Pleuromutilin (**1**), an antibiotic isolated from *Pleurotus mutilus* and other basidiomycetes, was first reported by Kavanagh in 1951.[2] Derivatives of **1** are currently used as important antimycoplasmal agents in veterinary medicine.[3] Structurally, pleuromutilin is a most intriguing diterpene due to its intricate tricyclic skeleton and rare eight-membered ring.[4-6] Unusual chemistry arising from these structural features has been described by Arigoni in his detailed elucidation of the biogenesis of **1**.[4,7] In this communication we report the first total synthesis of (±)-pleuromutilin (**1**) by an efficient stereoselective route.



pleuromutilin (**1**), R = COCH$_2$OH
mutilin (**2**), R = H

Our approach to this tricyclic ring system is based on a sequential Michael strategy which produces in one step the indane nucleus with four of the eight stereocenters of **1**.[8] Thus, treatment of the kinetic enolate of **3**[8] at -70 °C in THF with **4**[9,10] gave the sequential Michael adduct **5** (mp 73-74 °C) as the sole product in 62% yield[11] (see Chart I for structures). Homologation of **5** to the α,β-unsaturated methyl ketone **6** was carried out by means of a four-step sequence. Selective addition of vinyl lithium (THF-Et$_2$O, -40 °C, 67%), followed by oxidative rearrangement (PCC, CH$_2$Cl$_2$, 79%)[12] produced the α,β-unsaturated aldehyde, which was then transformed to **6** by methyl lithium addition (THF, -93 to -80 °C, 82%) and subsequent allylic oxidation (MnO$_2$, CH$_2$Cl$_2$, 88%).[13] Catalytic hydrogenation of **6** (H$_2$, 10% Pd/Al$_2$O$_3$, MgO, 25:1 CH(OCH$_3$)$_3$-EtOAc, 1 atm)[14] gave the desired

---

* Address Correspondence to this author at E. R. Squibb & Sons, Inc., P.O. Box 4000, Princeton, NJ 08540.

(1) Abstracted from: Gibbons, E. G. Ph.D Thesis, Harvard University, Cambridge, Massachusetts, 1982.

(2) (a) Kavanagh, F.; Hervey, A.; Robbins, W. J. *Proc. Natl. Acad. Sci. U.S.A.* **1951**, *37*, 570. *Ibid.* **1952**, *38*, 555. (b) For a review of terpenoid metabolites of mushrooms and related basidiomycetes, see: Ayer, W. A.; Browne, L. M. *Tetrahedron* **1981**, *37*, 2199.

(3) Dreyfuss, J.; Singhvi, S. M.; Shaw, J. M.; Egli, P.; Ross, J. J., Jr.; Czok, R.; Nefzger-Biessels, M.; Battig, F.; Schuster, I.; Schmook, F. *J. Antibiot.* **1979**, *32*, 496 and references therein. Riedl, K. *Ibid.* **1976**, *29*, 132 and references therein.

(4) Arigoni, D. *Gazz. Chim. Ital.* **1962**, *92*, 884; *Pure Appl. Chem.* **1968**, *17*, 331. See also: Nageli, P.; Dissertation, ETH 3206, 1961; Bonavia, G. Dissertation, ETH 4189, 1968; Hasler, H. Dissertation, ETH 6359, 1979.

(5) Birch, A. J.; Cameron, O. W.; Holzapfel, C. W.; Rickards, R. W. *Chem. Ind. (London)* **1963**, *374*. Birch, A. J.; Holzapfel, C. W.; Rickards, R. W. *Tetrahedron* **1966**, *22*, 359.

(6) X-ray structure: Dobler, M.; Dürr, B. G. *Cryst. Struct. Commun.* **1975**, *4*, 259.

(7) See also ref 5 for a discussion of the biogenesis of **1**.

(8) Gibbons, E. G. *J. Org. Chem.* **1980**, *45*, 1540.

(9) **4** was synthesized in four steps from 3-methyl-2-cyclohexen-1-ol: (i) PhCH$_2$Br, KH, THF; (ii) O$_3$, CH$_2$Cl$_2$-MeOH, -78 °C; (iii) (MeO)$_3$P, -78 °C; (iv) 5% aqueous NaOH, Et$_2$O, 24 h, 50% overall.

(10) Satisfactory combustion analyses and spectroscopic data were obtained for all new compounds with the exceptions of **6-8** and **13-25** where the elemental composition was confirmed by high-resolution mass spectrometry. IR and NMR spectra are available as supplementary material.

(11) See ref 8 for a discussion of stereochemistry in the sequential Michael reaction. The stereochemistry at C(3) was later established by correlation with reduced derivatives of mutilin (**2**).[5]

(12) Dauben, W. G.; Michno, D. M. *J. Org. Chem.* **1977**, *42*, 682.

(13) Fatiadi, A. J. *Synthesis* **1976**, 65. Attenburrow, J. et al. *J. Chem. Soc.* **1952**, 1094.

(14) The use of MgO buffer prevented loss of the benzyl group by hydrogenolysis, while the CH(OCH$_3$)$_3$-EtOAc solvent mixture provided the best stereoselectivity.

0002-7863/82/1504-1767$01.25/0