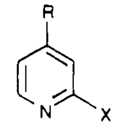
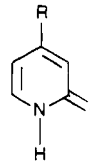
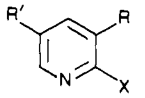
with quinoline (**3**), producing, almost instantaneously, 2-acetoxyquinoline (**4**) in higher than 90% yield. In both cases raising the temperature of the reaction to 0 °C did not change its outcome.



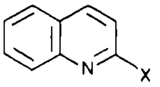
1: R = X = H
2: R = H; X = OAc
5: R = Me; X = H
6: R = Me; X = OAc
7: R = COPh; X = H
8: R = COPh; X = OAc



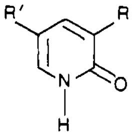
9: R = Me
10: R = COPh



11: R = Me; R′ = X = H
12: R = Me; R′ = H; X = OAc
13: R = H; R′ = Me; X = OAc
16: R = COPh; R′ = X = H



3: X = H
4: X = OAc

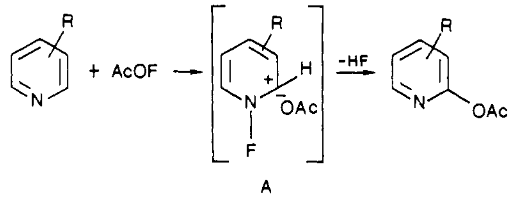


14: R = Me; R′ = H
15: R = H; R′ = Me

Pyridine substituted at the 4-position, such as 4-methylpyridine (**5**), reacted with AcOF to form 2-acetoxy-4-methylpyridine (**6**) in 75% yield, though a higher temperature, −10 °C, was required. Similar results were obtained with 4-benzoylpyridine (**7**) which after a short reaction with acetyl hypofluorite was transformed to the previously unknown 2-acetoxy derivative **8** (oil) in 90% yield. Both **6** and **8** were quantitatively hydrolyzed with water at 50 °C to the corresponding pyridones **9**[9] and **10**, mp 160 °C (from EtOAc).

When the substitutent was chosen to be in the 3-position, as in 3-methylpyridine (**11**), a 1:1 mixture of 2- and 5-acetoxy-3-methylpyridines (**12** and **13**)[10] was formed in 75% yield. These acetoxy derivatives were separated and then quantitatively hydrolyzed to the corresponding pyridones **14** and **15**.[9]

It is unlikely that the substitution proceeds via any radical pathway, since the addition of radical inhibitors or initiators such as nitrobenzene or benzoyl peroxide does not affect the outcome of the reaction. We believe that the first step is an attack of the electrophilic fluorine of the AcOF on the nitrogen lone pair electrons producing the ion pair A. Subsequent collapse of the ion pair and elimination of HF is strongly encouraged by the restoration of the aromaticity of the heterocyclic ring. Similar reaction pathway was found with electrophilic aromatic fluorination using AcOF.[7a]



A

This mechanism is supported by several observations. First, no acetoxylation was observed with 2-substituted pyridine rings. In the case where an electron-donating substituent is present as in 2-methyl- or 2-methoxypyridine, a ready addition across the region between the electron-donating substituent and the nitrogen takes place, but then no easy pathway for elimination of HF is possible and the resulting reactive diene system reacts further with AcOF to give many unidentified products. On the other hand, an electron-withdrawing group at the same position, as with 2-chloro- or 2-cyanopyridine, completely inhibits the reaction by reducing the basicity of the nitrogen and preventing the first addition step and there is full recovery of the starting material. The mechanism is also in accordance with the reaction of 3-benzoylpyridine (**16**) with AcOF, where the ^{19}F NMR has a signal at −63.4 ppm which is very characteristic to *N*-fluoropyridone derivatives.[11] It should also be mentioned that similar electrophilic attack of F_2 on the nitrogen atom of the pyridine ring was successfully used for fluorination purposes by Purrington[11] and Umemoto.[12]

In conclusion, it seems that the remarkable synthetic potential of elemental fluorine includes not only the ability to construct fluorine-containing compounds, but also to facilitate other difficult chemical transformations.

Acknowledgment. We thank the Fund for Basic Research administrated by the Israel Academy of Science and Humanities for supporting this research.

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(10) Oae, S.; Kozuka, S. *Tetrahedron* **1964**, *20*, 2691.

(11) Purrington, S. T.; Jones, W. A. *J. Org. Chem.* **1983**, *48*, 762. Purrington, S. T.; Jones, W. A. *J. Fluorine Chem.* **1984**, *26*, 43.

(12) Umemoto, T.; Tomita, K. *Tetrahedron Lett.* **1986**, *27*, 3271. Umemoto, T.; Kawada, K.; Tomita, K. *Tetrahedron Lett.* **1986**, *27*, 4465.

Linear Free Energy Relationships for Excimers

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We wish to report a linear free energy relationship, correlating ΔH and ΔS for intramolecular excimer formation. Such linear free energy relationships have been found for a great variety of chemical and physical phenomena.[1] However, for excited-state complexes, in contrast to electron donor–acceptor complexes in the electronic ground state,[2] linear ΔH–ΔS relationships have not previously been observed.

For intermolecular excimers and other excited state complexes ΔS has been assumed to be independent of the system with a value of the order of −80 J K^{-1} mol^{-1}, which was thought to be the expectation value for a molecular association process.[3] This assumption was based on the apparent constancy of the ΔS data for excimers in the literature.[3a,4] It also fitted the notion that a major contribution to ΔS for excimers comes from the reduction of the number of the degrees of freedom when an excimer, having two molecules in a rigid sandwich structure, is formed from two spatially uncorrelated molecules. It then appeared to be self-evident that intermolecular excimers and exciplexes with ΔH values smaller than −24 kJ/mol would not be easily detectable at room temperature, as under these conditions ΔG would be positive. However, as a notable exception to this expectation, efficient exciplex formation (k_a = 7.1 × 10^9 s^{-1} at 25 °C) was recently observed for perylene/Ag$^+$ in methanol, with ΔH = −4 kJ/mol and ΔS = +22 J K^{-1} mol^{-1}.[5] The possibility that even weakly stabilized complexes in the excited state can be readily formed will be discussed on the basis of the ΔH–ΔS compensation relation to be presented here.

In Figure 1, the values for ΔH and ΔS for the intramolecular excimers of a series of dipyrenylalkanes in a variety of alkane solvents and in toluene are plotted. These compounds form ex-

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(1) (a) Leffler, J. E. *J. Org. Chem.* **1955**, *77*, 334. (b) Exner, O. *Prog. Phys. Chem.* **1973**, *10*, 411. (c) Giese, B. *Acc. Chem. Res.* **1984**, *17*, 438. (d) Doan, P. E.; Drago, R. S. *J. Am. Chem. Soc.* **1984**, *106*, 2772.

(2) (a) Briegleb, G. *Elektronen-Donator-Acceptor-Komplexe*; Springer: Berlin, 1961. (b) Person, W. B. *J. Am. Chem. Soc.* **1962**, *84*, 536. (c) Foster R. *Organic Charge-Transfer Complexes*; Academic: New York, 1969. (d) Mulliken, R. S.; Person, W. B. *Molecular Complexes*; Wiley: New York, 1969.

(3) (a) Stevens, B. *Adv. Photochem.* **1971**, *8*, 161. (b) Zachariasse, K. A. Ph.D. Thesis, Free University, Amsterdam, 1971. (c) Klöpffer, W. In *Organic Molecular Photophysics*: Birks, J. B., Ed.; Wiley: New York, 1973; Vol. 1.

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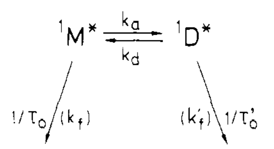
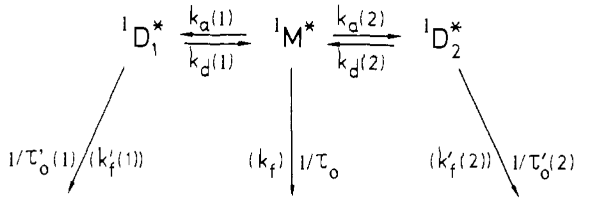
(5) Läufer, A. G. E.; Dreeskamp, H.; Zachariasse, K. A. *Chem. Phys. Lett.* **1985**, *121*, 523.

0002-7863/87/1509-3790$01.50/0

Scheme I



Scheme II



cimers according to two kinetic schemes, Schemes I and II. With 1,3-di(2-pyrenyl)propane (2Py(3)2Py), 1,3-di(2-pyrenyl)butane, the meso and racemic diastereoisomers of 2,4-di(2-pyrenyl)pentane (*meso-* and *rac-*2DPP), and 1,16-di(1-pyrenyl)hexadecane (1Py(16)1Py), excimer formation can be described by Scheme I, with one excited-state monomer $^1M^*$ and one excimer $^1D^*$,[6] with the (first-order) rate constants k_a (excimer formation), k_d (thermal excimer dissociation), k_f (monomer fluorescence), and k'_f (excimer fluorescence), and with the fluorescence lifetimes τ_0 (monomer) and τ'_0 (excimer). Scheme I is similar to the one valid for intermolecular excimer and exciplex formation, such as with pyrene and perylene/Ag$^+$.[4,5]

Intramolecular excimer formation with 1,3-di(1-pyrenyl)-propane (1Py(3)1Py), however, could only be described by the more complex Scheme II, comprising two structurally different excimers $^1D_1^*$ and $^1D_2^*$ in addition to one excited-state monomer.[6]

By determining all rate constants and lifetimes appearing in the Schemes I and II as a function of temperature, utilizing time-correlated single-photon counting measurements, the activation energies E_a (of k_a) and E_d (of k_d), as well as the preexponential factors k_a^0 and k_d^0, have been obtained.[6] From these entities the enthalpy difference $\Delta H = E_a - E_d$ and the entropy difference $\Delta S = R \ln (k_a^0/k_d^0)$ were deduced.

The ΔH–ΔS data points in Figure 1 lie on two straight lines, L1 and L2. For each of the different compounds the values depend on the nature of the solvent, contrary to what was assumed previously.[3a,4] Focusing attention on 1Py(3)1Py, it is seen that the data for the two excimers $^1D_1^*$ and $^1D_2^*$ lie on L1 and L2, respectively. The data points for the excimers of 2Py(3)2Py and of *meso-* and *rac-*2DPP also lie on L1, whereas the ΔH–ΔS values for 1Py(16)1Py lie on L2. The slope of a linear plot of ΔH vs. ΔS gives an isokinetic temperature $\beta = \delta\Delta H/\delta\Delta S$, at which temperature the rate constant ratio k_a/k_d of excimer formation over dissociation (i.e., the equilibrium constant) remains unchanged.[7] From the slopes of the straight lines in Figure 1, equal to $1/\beta$, the following isokinetic temperatures are obtained: 330 K (L1) and 304 K (L2), with $\Delta G(\mathrm{L1}) = -11$ kJ/mol and $\Delta G(\mathrm{L2}) = -7$ kJ/mol at these temperatures. As is generally the case, these isokinetic temperatures and their corresponding ΔG values do not have a straightforward physical interpretation.[1]

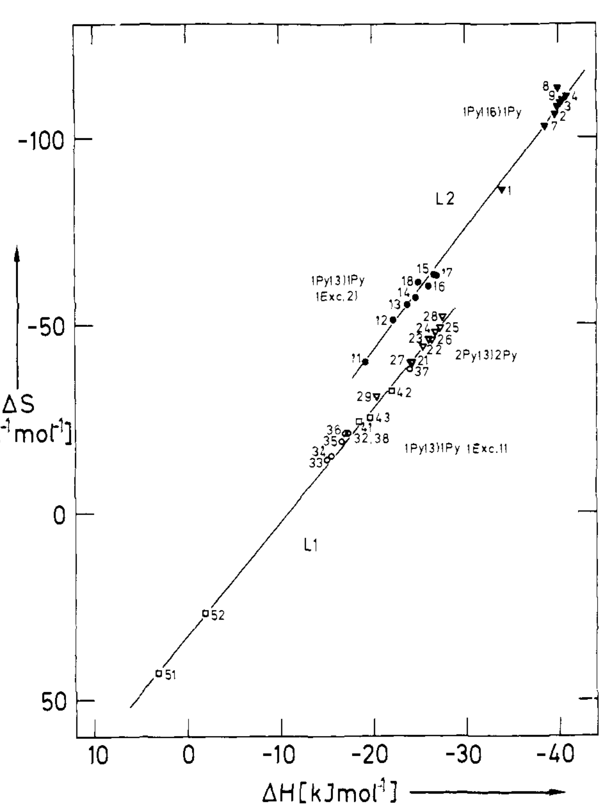


Figure 1. Plot of ΔS vs. ΔH for intramolecular excimer formation with a number of dipyrenylalkanes in various solvents. (a) 1,16-Di(1-pyrenyl)hexadecane: (1) *n*-pentane; (2) *n*-hexane; (3) *n*-heptane; (4) *n*-decane; (6) *n*-hexadecane; (7) liquid paraffin (80 °C < T < 140 °C); (8) toluene; (9) methylcyclohexane. (b) 1,3-Di(1-pyrenyl)propane, excimer $^1D^*_2$: (11) *n*-pentane; (12) *n*-hexane; (13) *n*-heptane; (14) *n*-decane; (15) *n*-dodecane; (16) *n*-hexadecane; (17) liquid paraffin (50 °C < T < 80 °C); (18) toluene. (c) 1,3-Di(1-pyrenyl)propane, excimer $^1D^*_1$: (32) *n*-hexane; (33) *n*-heptane; (34) *n*-decane; (35) *n*-dodecane; (36) *n*-hexadecane; (37) liquid paraffin (80 °C < T < 145 °C); (38) toluene. (d) 1,3-Di(2-pyrenyl)propane: (21) *n*-pentane; (22) *n*-hexane; (23) *n*-heptane and *n*-hexadecane; (24) *n*-nonane and *n*-decane; (25) *n*-dodecane; (26) *n*-octane; (27) liquid paraffin (80 °C < T < 140 °C); (28) toluene; (29) methylcyclohexane. (e) *rac*-2,4-Di(2-pyrenyl)pentane: (41) methylcyclohexane; (42) toluene; (43) *n*-octane. (f) *meso*-2,4-Di(2-pyrenyl)-pentane: (51) methylcyclohexane; (52) toluene. (g) 1,3-Di(2-pyrenyl)-butane: (61) methylcyclohexane.

At this point, a discussion of excimer structure is necessary.[6a] On the basis of the spectral similarity between the excimer fluorescence bands of pyrene in fluid solution (lifetime $\tau'_0 \sim 60$ ns)[4,6e] and in single crystals, the excimer configuration has been taken to be identical in the two media: a parallel sandwich structure where the pyrenes are shifted along their long axis by one aromatic C–C bond length.[4] On the other hand, for the intramolecular excimer ($\tau'_0 \sim 150$ ns) of 2Py(3)2Py, the trimethylene chain dictates a symmetric configuration for the two symmetrically substituted pyrenyl groups.[6] The occurrence of this symmetric configuration for the two pyrene moieties is supported by the observation that the excimer lifetime and the excimer fluorescence band of 2Py(3)2Py are similar to those of the symmetric [3.3](2,7)pyrenophane.[6b,8] For 1Py(3)1Py, where two excimers are detected as mentioned above, one of the excimers ($^1D^*_2$ with $\tau'_0(2) \sim 70$ ns, similar to that of pyrene) is supposed to have an asymmetric configuration, whereas the other excimer ($^1D^*_1$ with $\tau'_0(1) \sim 150$ ns) will have a symmetric structure.[6a] Finally, for 1Py(16)1Py ($\tau'_0 \sim 60$ ns)[6d,9] the alkane chain appears to be sufficiently long to form exclusively the more stable[4,6] asymmetric excimer configuration. These considerations are supported by $S_n \leftarrow S_1$ excited state absorption measurements.[9]

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(6) (a) Zachariasse, K. A.; Busse, R.; Duveneck, G.; Kühnle, W. *J. Photochem.* **1985**, *28*, 237. (b) Zachariasse, K. A.; Duveneck, G.; Kühnle, W. *Chem. Phys. Lett.* **1985**, *113*, 337. (c) Zachariasse, K. A.; Duveneck, G.; Kühnle, W.; Reynders, P.; Striker, G. *Chem. Phys. Lett.* **1987**, 133, 390. (d) Duveneck, G. Ph.D. Thesis, University of Göttingen, 1986. (e) Zachariasse, K. A.; Busse, R. In *Excited State Probes in Biochemistry and Biology*; Szabo, A., Ed.; Plenum: New York, in press. (f) Zachariasse, K. A.; Busse, R.; Duveneck, G.; Kühnle, W. In *Excited State Probes in Biochemistry and Biology*; Szabo, A., Ed.; Plenum: New York, in press. (g) Zachariasse, K. A.; Busse, R.; Schrader, U.; Kühnle, W. *Chem. Phys. Lett.* **1982**, *89*, 303. (h) Busse, R. Ph.D. Thesis, University of Göttingen, 1984.

(7) Linear free energy relationships often connect the activated complex parameters $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$. From the slope of the data points showing such a relationship, the so-called "isokinetic temperature" can be derived: $\beta = \delta\Delta H^{\ddagger}/\delta\Delta S^{\ddagger}$. At this temperature all systems have the same value for $\Delta G^{\ddagger}$ and hence have identical rate constants for the process for which $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ were calculated.

(8) Staab, H. A.; Riegler, N.; Diederich, F.; Krieger, C.; Schweitzer, D. *Chem. Ber.* **1984**, *117*, 246.

(9) Zachariasse, K. A.; Duveneck, G., unpublished results.

The conclusions on excimer symmetry presented above, which are based on the similarity of the excimer lifetimes, are fully supported by the correlation of the data in Figure 1. In this Figure the data points for excimer $^1D^*_1$ of 1Py(3)1Py, for which a symmetric structure was assumed, have the same linear ΔH vs. ΔS correlation as that of the symmetric excimers of 2Py(3)2Py and *meso*- and *rac*-2DPP (line L1). The ΔH–ΔS data of the second, asymmetric, excimer $^1D^*_2$ of 1Py(3)1Py lie on the same line as those of the asymmetric excimer of 1Py(16)1Py (line L2). It can therefore be concluded that the two straight lines in Figure 1 differentiate the data according to excimer symmetry.

Further, of special interest is the observation that in the case of *meso*-2DPP in methylcyclohexane, which has a positive value for ΔH (Figure 1, point 51), efficient excimer formation occurs (k_a = 5.6 × 10^8 s^{-1} at 25 °C),[6c] the reaction being driven by entropy.[5]

An important general conclusion to be derived from the ΔH–ΔS relationship for excimers presented here is that the formation of weakly stabilized complexes in the excited state (even those with positive ΔH) cannot be ruled out a priori. Their small ΔH values are compensated by a proportionally less negative or even positive value for ΔS. This is especially important in the ongoing discussions on the existence of triplet excimers.[10] Triplet excimers certainly will have small absolute ΔH values, as locally excited triplet states do not lead to a stabilization by exciton interaction.[11,12] In addition, the charge resonance interaction between the states $^3A^*A$ and A^+A^- mostly is weak, due to the relatively large energy difference between the two states, as compared to singlet excimers. Because of the ΔH–ΔS compensation, such weakly stabilized triplet excimers can nevertheless be formed. As an example, for the triplet excimer of 1,3-di(9-phenanthryl)propane in *n*-decane, a ΔH of −11 kJ/mol was found, with a ΔS value of −23 J K^{-1} mol^{-1}.[6f–h]

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[10] (a) Nickel, B.; Rodriguez Prieto, M F. *Z. Phys. Chem.* (*Munich*) **1986**, *150*, 31 and references cited therein. (b) Lim, E. C. *Acc. Chem. Res.* **1987**, *20*, 8.

[11] Mc Glynn, S. P.; Armstrong, A. T.; Azumi, T. In *Modern Quantum Chemistry*; Sinanoglu, O., Ed.; Academic: New York, 1965; Vol. 3.

[12] Weller, A. In *The Exciplex*; Gordon, M.; Ware, W. R., Eds.; Academic: New York, 1975.

A Cis Hydroxyamination Equivalent: Application to the Synthesis of (−)-Acosamine

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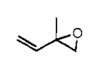
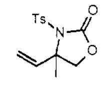
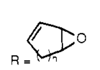
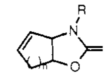
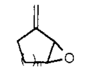
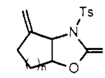
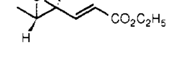
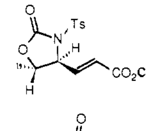
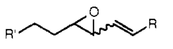
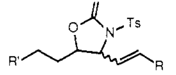
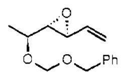
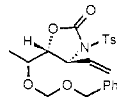
Diastereoselective introduction of heteroatoms constitutes an important challenge in complex synthesis. Recent interest in amino sugars[1–3] has drawn attention to the process of hydroxyamination.[4]

Table I. Pd-Catalyzed Oxazolidin-2-one Synthesis

entry	vinyl epoxide	isocyanate	product	yield
1		TsNCO		79%
		RNCO		
2	n = 1	R = Ph	n = 1, R = Ph	78%
3	n = 2	R = Ph	n = 2, R = Ph	90%
4	n = 2	R = –⟨◯⟩–OCH$_3$	n = 2, R = –⟨◯⟩–OCH$_3$	92%
5	n = 2	R = Ts	n = 2, R = Ts	100%
		TsNCO		
6	n = 1		n = 1	87%
7	n = 2		n = 2	63%
8		TsNCO		60%
		TsNCO		
9	R = H, R' = Ph		R = H, R' = Ph	92%
10	R = CH$_3$, R' = Ph		R = CH$_3$, R' = Ph	74%
11	R = H, R' = n-C$_{10}$H$_{21}$		R = H, R' = n-C$_{10}$H$_{21}$	94%
12		TsNCO		100%

The ready availability of epoxides in enantiomerically pure form from olefins[5] makes such intermediates particularly useful in achieving a net hydroxyamination of olefins.[6,7] Reaction of vinyl epoxides with nitrogen nucleophiles in the presence of Pd(0) catalysts leads to 1,4-substitution (eq 1, path a).[8] We therefore sought a complementary regiochemistry, i.e., a vicinal hydroxyamination (eq 1, path b), based upon the notion of tethering the nucleophile to the oxygen of the leaving group as in eq 1, path c. The conceptual problems with this approach are (1) the efficacy of trapping the initial zwitterion with isocyanates prior to its unimolecular decomposition and (2) the possibility of O- rather than N-alkylation if the zwitterion can be intercepted by the isocyanate.[9] Indeed, the thermal reaction of vinyl epoxides with

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