species the decompositions occur at least 150° lower than in the solution phase.

Difluorocarbene (CF_2) is also a decomposition product as shown by the presence of TFE, and trapping by isobutylene. The CF_2 is not formed by disproportionation of CF_3 radicals since tetrafluoromethane is not a product while fluoride ion is. It is interesting that no TFE or polymer was formed in the pivalaldehyde experiment, and yet a large yield of fluoride was found. Perhaps the aldehyde scavenges the CF_2 formed. At this time we have no good explanation as to why the fluoride and iodide yields are so high when carbonyl compounds are used as additives.

The following scheme explains the major pathways.

$$\mathrm{CF_3I + Zn \longrightarrow \underset{I}{CF_3ZnI}}$$

$$\mathrm{I + H_2O \xrightarrow{-50\ to\ -100^\circ} CF_3H + Zn(OH)I}$$

$$\mathrm{I \xrightarrow{-80^\circ} :CF_2 + ZnFI}$$

or

$$\mathrm{I \xrightarrow{-80^\circ} \cdot CF_3 + \cdot ZnI}$$

$$\mathrm{2CF_3 \longrightarrow CF_3CF_3}$$

$$\mathrm{\cdot ZnI + CF_3I \longrightarrow ZnI_2 + \cdot CF_3}$$

$$\mathrm{2CF_2 \longrightarrow TFE}$$

$$\mathrm{\cdot CF_3 + TFE \longrightarrow polymer}$$

$$\mathrm{\cdot CF_3 + RH \longrightarrow CF_3H + R\cdot}$$

After appropriate hydrolysis techniques, we determined that I did not add to the carbonyl bonds of the additives to yield alcohols.

Both CH_3I and CF_3Br were much less reactive with zinc atoms than CF_3I.

Further investigations of other metal atoms with saturated and unsaturated fluorocarbons are in progress.

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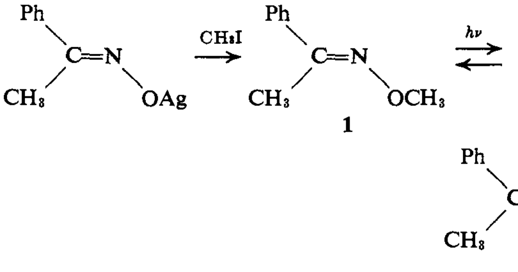
Photoisomerization about the Carbon–Nitrogen Double Bond of an Oxime Ether

Sir:

While photochemical reactions have been observed with several systems possessing a C–N double bond,[1–12] a more frequently encountered phenomenon for simple imines is a high rate and efficiency of radiationless decay of the excited state.[13] The facile deactivation of the imine chromophore can be attributed to rotation about the π bond in the excited state, thereby allowing for dissipation of electronic energy.[14] The photo[15–20] and thermal[21–23] interconversions of the syn and anti isomers of imines are a subject of long-standing interest. Recent investigations into the factors influencing the ease of isomerization about the C–N double bond have shown that the inversion barrier is remarkably sensitive to attached substituent groups.[21–23] The great configurational stability of oxime ethers stands in striking contrast to the behavior of *N*-aryl- and alkylimines.[21] These oxime ethers are attractive candidates for mechanistic photostudies since the presence of the methoxyl group drastically reduces the rate of thermal interconversion ($k < 10^{-13}$ at 60°). In the present communication we report on some aspects of the direct and sensitized isomerization of the syn and anti isomers of acetophenone oxime *O*-methyl ether.

The *anti-O*-methyl ether of acetophenone oxime (**1**) was synthesized by O-methylation of the silver salt of acetophenone oxime (nmr (CCl_4) τ 7.91 (s, 3 H), 6.08 (s, 3 H)). The corresponding syn isomer **2** was prepared by irradiation of **1** in pentane using a 2537-Å source (nmr (CCl_4) τ 7.88 (s, 3 H), 6.25 (s, 3 H)). The two isomers could be readily separated by vapor phase chromatography and their thermal stability was established by heating each isomer separately at 150° for 168 hr (in benzene) and noting the absence of isomerization. The ultraviolet absorption spectra of both the syn and anti forms resembled that of α-methylstyrene. The 0–0 band of the syn isomer appears at 2850 Å (100 kcal/mol), while that of the anti form appears at 2900 Å (98 kcal/mol). These absorptions can be attributed to a π–π* transition; no absorption corresponding to a lower energy n–π* transition was observed.



1

2

The photostationary state ratio obtained by direct irradiation in a pentane solution at 2537 Å (syn/anti) was 2.21 ± 0.03. The quantum yield for syn → anti isomerization at 2537 Å was 0.43 ± 0.02 in the 4–5% reaction range, while that for anti → syn was 0.48 ±

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0.02. The photostationary state obtained in the direct irradiation should be given by the following expression (eq 1).[24] With the available data,[25] the photo-

$$\frac{[\text{syn}]}{[\text{anti}]} = \frac{\epsilon_{\text{anti}}[\Phi_{\text{anti}\rightarrow\text{syn}}]}{\epsilon_{\text{syn}}[\Phi_{\text{syn}\rightarrow\text{anti}}]} \qquad (1)$$

stationary state was calculated to be 2.40 ± 0.3, which was well within the experimental limits of the observed value. It is interesting to note that the direct photoisomerization could not be quenched by high (*ca.* 3 *M*) concentrations of piperylene. This is indicative of reaction from a singlet state or from the triplet manifold at a rate exceeding diffusional control.

Photoisomerization about the C–N double bond can also be induced by triplet excitation. Various sensitizers with known triplet energies were employed to reach a sensitized photostationary state[26] (see Figure 1). The plot shows several features[27] comparable to those found in the study of stilbenes,[24] namely (1) a high-energy region in which the stationary state ratio is *ca.* 1.5, (2) a gradual increase in the syn/anti ratio from 72 down to 59 kcal of triplet energy, and (3) a sharp decrease from 59 down to 54 kcal. The latter two observations can be satisfactorily explained by nonvertical excitation of the acceptor.

The quantum yields for the sensitized isomerization, using three high-energy sensitizers, are summarized in Table I. At the oxime ether concentrations used in these experiments (0.03–0.13 *M*), the quantum yields were found to be independent of anti oxime concentration and only slightly dependent on syn concentration.

Table I. Quantum Yields for Isomerization

Starting material (*M*)	Sensitizer	% conversion	Φ
Syn (0.03)		4–5	0.43 ± 0.02
Anti (0.03)		4–5	0.48 ± 0.04
Syn (0.03)	Acetophenone	8–9	0.30 ± 0.01
Anti (0.03)	Acetophenone	8–9	0.33 ± 0.01
Syn (0.06)	Acetophenone	9–10	0.34 ± 0.02
Anti (0.06)	Acetophenone	9–10	0.33 ± 0.01
Syn (0.13)	Acetophenone	9–10	0.36 ± 0.02
Anti (0.13)	Acetophenone	9–10	0.32 ± 0.01
Syn (0.03)	*p*-Methoxyacetophenone	8–9	0.36 ± 0.02
Anti (0.03)	*p*-Methoxyacetophenone	8–9	0.34 ± 0.01
Syn (0.03)	Propiophenone	8–9	0.30 ± 0.02
Anti (0.03)	Propiophenone	8–9	0.33 ± 0.01

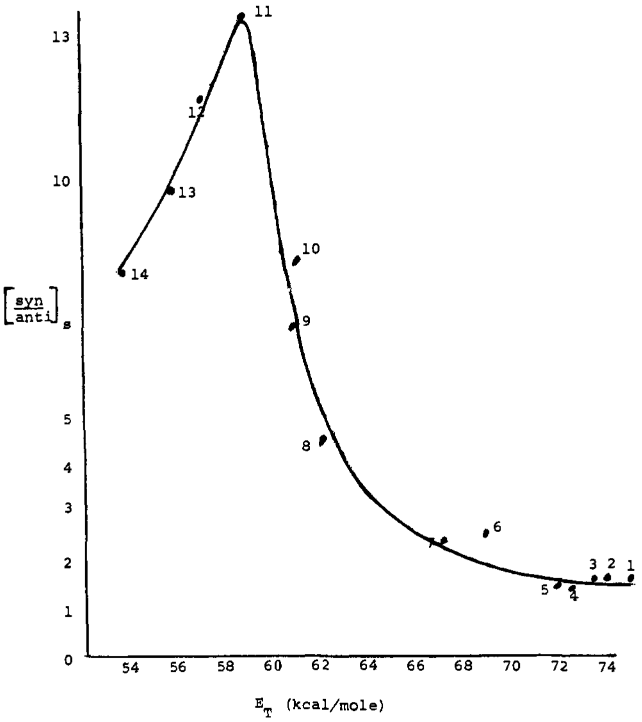

Figure 1. Sensitized isomerization of oxime ethers **1** and **2**: 1, propiophenone; 2, acetophenone; 3, isobutyrophenone; 4, benzaldehyde; 5, 4-methoxyacetophenone; 6, benzophenone; 7, triphenylene; 8, phenanthrene; 9, 4-acetylbiphenyl; 10, naphthalene; 11, 2-acetonaphthone; 12, chrysene; 13, 1-napthaldehyde; 14, benzil.

The standard formula for predicting the sensitized state, *i.e.*, eq 2, predicts a photostationary state value of

$$\frac{[\text{syn}]_s}{[\text{anti}]_s} = \frac{\Phi_{\text{anti}\rightarrow\text{syn}}}{\Phi_{\text{syn}\rightarrow\text{anti}}} \qquad (2)$$

syn/anti (at 0.03 *M*) = 1.10 ± 0.15 for acetophenone, syn/anti = 0.94 ± 0.13 for *p*-methoxyacetophenone, and syn/anti = 1.10 ± 0.10 for propiophenone. It is noteworthy that the predicted values are not in agreement with the observed values of 1.64 ± 0.04 for acetophenone, 1.35 ± 0.07 for *p*-methoxyacetophenone, and 1.66 ± 0.05 for propiophenone. Equation 2 is valid only if the rate constants for quenching sensitizer triplets by the two isomers are the same. This appears not to be the case and therefore the data must be treated by the more rigorous expression (eq 3),

$$\frac{\Phi_{\text{a}\rightarrow\text{s}}}{\Phi_{\text{s}\rightarrow\text{a}}} = \frac{[\text{syn}]_s[k_4 + k_6[\text{syn}]]}{[\text{anti}]_s[k_4 + k_5[\text{anti}]]} \qquad (3)$$

where k_4 represents both the radiationless and radiative decay of sensitizer and k_5 and k_6 represent the quenching rates for the anti and syn isomers. Since the quantum efficiencies were determined at identical oxime ether concentrations and since Φ is more or less independent of oxime concentration, eq 3 may be approximated by eq 4. The "excitation ratio"[28,29] k_5/k_6

$$\frac{[\text{syn}]_s}{[\text{anti}]_s} = \frac{\Phi_{\text{a}\rightarrow\text{s}}k_5}{\Phi_{\text{s}\rightarrow\text{a}}k_6} \qquad (4)$$

is *ca.* 1.60 ± 0.1 (the anti isomer is a better triplet acceptor than the syn form) while the "decay ratio" is 1.0 ± 0.1. The deviation of the excitation ratio from unity may be a consequence of the fact that energy transfer from the high-triplet sensitizers to the syn isomer is not yet diffusion controlled.[30]

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[25] At 2537 Å, $\epsilon_{\text{anti}} = 1.09 \times 10^4$, $\epsilon_{\text{syn}} = 0.507 \times 10^4$.

[26] Each isomer was irradiated separately in pentane at 3130 Å. The isotopic composition changed with time and asymptotically approached the same photostationary composition.

[27] From Figure 1 we can approximate the triplet energy levels of both isomers as anti ($E_T \sim 59$ kcal) and syn ($E_T \sim 72$ kcal) if we assume that the syn energy level is the cause of the asymptotic behavior of the plot and the anti energy level is located at the maximum syn/anti ratio.

[28] This is only an approximation since the $\Phi_{\text{s}\rightarrow\text{a}}$ is somewhat dependent on the concentration of syn oxime.

[29] It is noteworthy that the anti isomer quenches acetophenone's phosphorescence emission more efficiently (*ca.* 1.5) than the syn isomer. This observation supports the contention that these isomers quench acetophenone's triplet with different rate constants.

If decay from a common twisted state is involved in the sensitized and unsensitized experiments, the photostationary state derived from direct irradiation should be related to that obtained with high-energy sensitizers in the following way

$$\frac{[\mathrm{syn}]_{\mathrm{s}}}{[\mathrm{anti}]_{\mathrm{s}}} = \frac{\epsilon_{\mathrm{anti}}\,[\Phi_{\mathrm{anti}\rightarrow\mathrm{syn}}]}{\epsilon_{\mathrm{syn}}\,[\Phi_{\mathrm{syn}\rightarrow\mathrm{anti}}]}$$

This relationship predicts a sensitized photostationary state of syn/anti = 2.36 ± 0.3 for acetophenone, 2.04 ± 0.2 for *p*-methoxyacetophenone, and 2.21 ± 0.2 for propiophenone. The calculated photostationary state values are greater than the observed values by a factor of *ca.* 1.4.[31]

The difference between the two numbers is an indication that crossing to triplets is not the sole fate of excited singlets, although the closeness of the values may indicate that the isomerization induced by direct irradiation is passing, in part, through the triplet.[31a] The finding of lower than predicted sensitized photostationary state values may also indicate that the identity of the intersystem crossing terms may not be the same for both isomers. Since the sum of the quantum yields, $\Phi_{\mathrm{syn}\rightarrow\mathrm{anti}} + \Phi_{\mathrm{anti}\rightarrow\mathrm{syn}}$, is less than unity it would appear that deactivation of singlet and/or triplet states of the oxime ethers includes radiationless decay processes[32] which proceed by paths not involving syn–anti isomerization. The source of inefficiency may be related to energy-degrading processes within a twisted excited state or may possibly involve relaxation of planar excited states in competition with decay of the twisted form. The inefficiency encountered with the sensitized experiments may indicate that not all acetophenone triplets are effective in generating a twisted imine triplet. Although radiationless paths which maintain geometric integrity are important to a degree, syn–anti isomerization provides the major route for deactivation of the excited imine state.

Acknowledgment. We wish to thank the National Science Foundation (Grant No. GP-24449) for financial support.

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(30) The fact that the $\Phi_{\mathrm{s}\rightarrow\mathrm{a}}$ is slightly dependent on syn oxime concentration is also compatible with a lower than diffusion-controlled quenching rate for the syn isomer.

(31) Similar discrepancies have been observed by deMayo and coworkers in the photoisomerization of benzaldoxime: H. Izawa, P. deMayo, and T. Tabata, *Can. J. Chem.*, 47, 51 (1969).

(31a) Note Added in Proof. These results are also consistent with a pathway that involves only excited singlets in the direct irradiation. This point will be discussed in greater detail in our full publication.

(32) Although no phosphorescence or fluorescence emission was observed from either isomer, these isomers did quench the phosphorescence emission of acetophenone (E_{T} = 73.6), benzophenone (E_{T} = 68.6), and phenanthrene (E_{T} = 62). The sensitization and phosphorescence studies confirm the fact that triplet energy occurs, and that transfer is possible even when the triplet energy of the sensitizer is insufficient to promote the oxime ether (1 or 2) to its spectroscopic triplet state.

(33) Alfred P. Sloan Foundation Fellow, 1968–1972.

(34) NDEA Title IV Fellow, 1967–1971.

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Effect of Nuclear Spin Relaxation on Intensity Patterns of Multiplet Spectra in Chemically Induced Dynamic Nuclear Polarization[1]

Sir:

Chemically induced dynamic nuclear polarization has been successfully explained in terms of nuclear spin state dependent triplet singlet intersystem crossing in correlated radical pairs.[2] According to this theory, the population N_n of the *n*th nuclear spin state of a product in a reacting system is given by eq 1, where

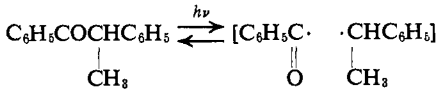
$$\frac{\mathrm{d}}{\mathrm{d}t}N_n = k_{\mathrm{r}}[{}^m\mathrm{M}]W_n + \sum_i (w_{i\rightarrow n}N_i - w_{n\rightarrow i}N_n) \quad (1)$$

$k_{\mathrm{r}}[{}^m\mathrm{M}]$ is the rate of radical pair formation from the precursor molecule M with multiplicity *m* and W_n is the nuclear spin state dependent probability of product formation from the pair. The $w_{i\rightarrow n}$ and $w_{n\rightarrow i}$ are the transition probabilities per unit time for the upward and downward relaxation processes connecting the nuclear spin levels *i* with level *n*. Neglecting the small nuclear Zeeman energy differences, we obtain eq 2 for the nmr

$$\frac{\mathrm{d}}{\mathrm{d}t}\,\mathrm{Int}_{nm} \propto \frac{\mathrm{d}}{\mathrm{d}t}(N_n - N_m) = k_{\mathrm{r}}[{}^m\mathrm{M}](W_n - W_m) - 2w_{mn}(N_n - N_m) + \sum_{i\neq m} w_{in}(N_i - N_n) - \sum_{i\neq n} w_{im}(N_i - N_m) \quad (2)$$

line intensity Int_{nm} with $w_{in} = w_{i\rightarrow n} = w_{n\rightarrow i}$. In all previous treatments it has been assumed that only the first term in eq 2 contributes to the relative intensities of CIDNP spectra. However, independent of the relaxation mechanism assumed, the last two relaxation terms in eq 2 never vanish for multilevel systems. *Therefore, relative line intensities in CIDNP multiplet spectra are only in part determined by the rates of product formation from the radical pair. Nuclear spin relaxation in the final product may play an important part.*[3]

Strong evidence for this fact is provided by the photoinduced α cleavage of phenyl α-phenylethyl ketone (I) to form the radical pair II.[4] Re-formation of I from



$$\underset{\mathrm{CH_3}}{\mathrm{C_6H_5COCHC_6H_5}} \overset{h\nu}{\rightleftarrows} [\mathrm{C_6H_5}\underset{\mathrm{O}}{\overset{}{\mathrm{C}}}\cdot \quad \cdot\underset{\mathrm{CH_3}}{\mathrm{CHC_6H_5}}]^3$$

I II

correlated radical pairs ("cage" recombination) occurs with strong emission of the benzylic methine proton quartet with line 1 (low-field line) missing (Figure 1b). Considering only the first term in eq 2, this fact leads to a *g* factor difference in II of $\Delta g = 3.6 \times 10^{-3}$.[5] It is important to note that this conclusion is independent

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(1) Supported by National Science Foundation Grant No. 18719X.

(2) (a) G. L. Closs, *J. Amer. Chem. Soc.*, 91, 4552 (1969); (b) R. Kaptein and L. J. Oosterhoff, *Chem. Phys. Lett.*, 4, 195, 214 (1969); (c) H. Fischer, *Z. Naturforsch. A*, 25, 1951 (1970); (d) G. L. Closs and A. D. Trifunac, *J. Amer. Chem. Soc.*, 92, 7227 (1970); (e) F. J. Adrian, *J. Chem. Phys.*, 54, 3912 (1971); (f) R. Kaptein, Ph.D. Thesis, Leiden, 1971; (g) G. L. Closs, *Spec. Lect. XXIIIrd Int. Congr. Pure Appl. Chem.*, 4, 19 (1971).

(3) The possible importance of relaxation effects in changing relative multiplet line intensities has recently been pointed out: M. Lehnig and H. Fischer, *Z. Naturforsch. A*, 25, 1963 (1970); R. Kaptein, see ref 1f, p 53.

(4) The triplet multiplicity of the reacting state was verified by effective quenching of the reaction with piperylene.

(5) Calculated with $|a_\alpha| = |a_\beta| \approx 17$ G for the hyperfine coupling constants in the α-phenylethyl radical; see D. W. Skelly, R. G. Hayes and W. H. Hamill, *J. Chem. Phys.*, 43, 2795 (1965).