[olefin] should give a straight line of gradient k_2/k_1 passing through the origin.

Scheme I

$$\begin{tikzcd} \text{EtOCON}_3 \arrow[r] & \text{singlet EtOCON} \arrow[r, "k_2", "\text{olefin}"'] \arrow[d, "k_1"] & \text{stereospecific product} \\ & \text{triplet EtOCON} \arrow[r, "\text{olefin}"'] & \text{nonstereospecific product} \end{tikzcd}$$

Values of X were estimated from the smooth curve obtained by plotting x *vs.* [olefin]; corrected values of x were similarly obtained. Using these derived values the graphs illustrated in Figures 2 and 3 were constructed. The linearity of these plots and the fact that they pass through the origin give evidence of the validity of our treatment and of the accuracy of our estimates for values of X, *viz.* 47 (80°) and 49% (120°) for *cis*-butene and 37 (80°) and 39% (120°) for *trans*-butene. The gradients, k_2/k_1, have the values 0.05 (80°) and 0.04 (120°) for the *cis* compound and 0.08 (80°) and 0.04 (120°) for the *trans* isomer and thus are of the same order of magnitude as those independently determined in a recent investigation.[7,10] Despite considerable uncertainty arising from possible experimental errors the general trend is quite clear. For both *cis*- and the *trans*-olefins k_2/k_1 decreases with increase of temperature thus indicating that the rate of intersystem crossing in carbethoxynitrene is temperature dependent and has an apparent activation energy greater than that for reaction of the singlet form with olefin. Our conclusions based on the reaction with anthracene are thus confirmed.[11]

The factors governing intersystem crossing have been the subject of considerable discussion and speculation.[9,12–16] In some cases involving excited states apparent activation energies have been detected.[15,17–20] In descriptive terms such an energy might represent that required to promote the singlet to the vibrational energy level corresponding to the point of intersection of the two potential energy surfaces.[6] Alternatively, if we imagine the probability of intersystem crossing to depend upon spin–orbit coupling with heavy atoms in the solvent, the activation energy might represent the barrier to sufficiently close contact between colliding molecules.[9,17]

Two other conclusions from our work deserve comment. At 80° singlet carbethoxynitrene reacts more rapidly with *trans*-butene-2 than with the *cis* isomer. This result, confirmed by separate competition experiments, accords with reactivity studies on dichlorocarbene[21] and appears reasonable in view of the probability that formation of the *cis*-aziridine from the *cis*-olefin involves a small increase in strain energy.[22] Secondly the values obtained for X indicate that reaction of triplet nitrene with olefin is not completely stereorandom. We suggest that spin inversion of the intermediate triplet biradical is sufficiently rapid to compete with bond rotation.

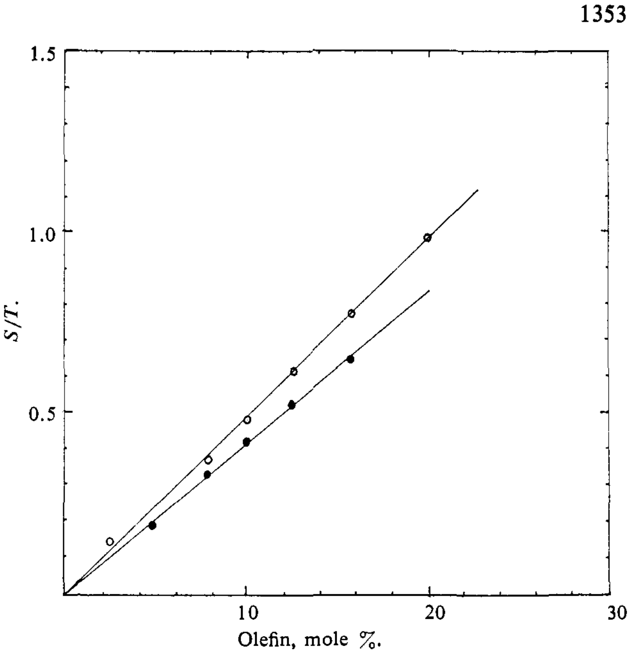

Figure 3. Ratio of products arising from singlet (S) and triplet (T) attack *vs.* olefin concentration for the reaction of *cis*-butene-2 with carbethoxynitrene at 80 (○) and 120° (●).

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(11) Since this work was completed a similar temperature dependence of product composition in the reaction of carbethoxynitrene with 4-methylpentene-2 has been noted.[10]

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(21) W. von E. Doering and W. A. Henderson, *ibid.*, **80**, 5274 (1958).

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A. L. J. Beckwith, J. W. Redmond
Organic Chemistry Department, University of Adelaide
Adelaide, South Australia 5000

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Spectrochemical-Electrochemical Evaluation of Kinetics Using Optically Transparent Electrodes

Sir:

We wish to report theoretical calculations and experimental results which demonstrate that kinetics of rapid homogeneous reactions following charge transfer may be evaluated spectrally using optically transparent electrodes. These electrodes, made from "doped" tin oxide coated glasses, have been applied to electrochemical studies using both normal transmission[1] and internal reflectance spectroscopy.[2] The latter allows the spectral monitoring of essentially the surface concentration of light-absorbing species. Transmission spectroscopy, on the other hand, is ideally suited to monitoring light-absorbing species in the diffusion layer and therefore can be advantageously applied to evaluating homogeneous chemical reactions which follow the charge-transfer step at the electrode.

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(1) T. Kuwana, R. K. Darlington, and D. W. Leedy, *Anal. Chem.*, **36**, 2023 (1964); J. W. Strojek and T. Kuwana, *J. Electroanal. Chem.*, in press.

(2) W. N. Hansen, R. A. Osteryoung, and T. Kuwana, *J. Am. Chem. Soc.*, **88**, 1062 (1966); *Anal. Chem.*, **38**, 1810 (1966).

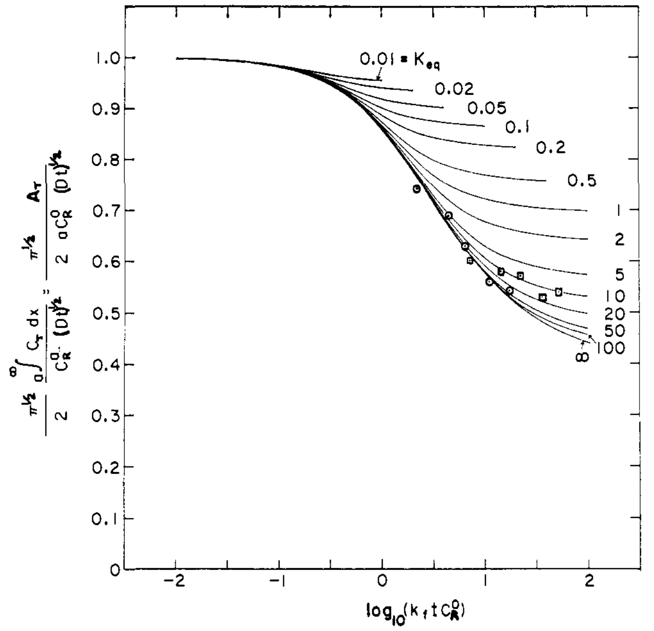

Figure 1. Normalized absorption *vs.* log ($k_f t C_R^0$) at various k_{eq} values. Circles are for 6.0 × 10^{-4} *M* *o*-tolidine. Squares are for 2.0 × 10^{-3} *M* *o*-tolidine.

In the simple case of an electrochemical reaction such as eq 1, where species T absorbs light, the absorbance

$$R \longrightarrow T + ne^- \qquad (1)$$

A_T during a diffusion-controlled chronoamperometric[3] experiment at a planar electrode can be easily calculated using a combination of Beer's law and the Cottrell equation[3] (eq 2 and 3) where a is the molar absorptivity

$$A_T = a_T\int_0^\infty C_T dx = a_T\int_0^t \frac{C_R^0 D_R^{1/2}}{(\pi t)^{1/2}} \qquad (2)$$

$$A_T = \frac{2a_T C_R^0 (D_R t)^{1/2}}{\pi^{1/2}} \qquad (3)$$

of T in l. mole^{-1} cm^{-1}, C_R^0 is the concentration of R in the bulk solution, and D_R is the diffusion coefficient. Any chemical reaction involving species T will produce a deviation in the normalized absorption

$$\frac{\pi^{1/2}A_T}{2a_T C_R^0 (D_R t)^{1/2}}$$

This will be illustrated for the mechanism

$$R \longrightarrow S + e^- \qquad (4)$$

$$S \longrightarrow T + e^- \qquad (5)$$

$$R + T \underset{k_b}{\overset{k_f}{\rightleftharpoons}} 2S \qquad (6)$$

where R undergoes two consecutive one-electron-transfer steps. Although the electrode potential during the pulse is adjusted so that $(C_R)_{x=0} = (C_S)_{x=0} = 0$, the relative concentrations of the three species in the diffusion layer are governed by the values of k_f and k_b. The redox potentials for reactions 4 and 5 and the equilibrium constant for reaction 6, $K_{eq} = k_f/k_b$, are, of course, thermodynamically related. Theoretical analysis of this problem was accomplished using a computer approach described by Feldberg and Auerbach.[4] The results, illustrated by the working curves in Figure 1, show the normalized absorption for species T at various values of K_{eq} as a function of the normalized rate parameter $k_f t C_R^0$.[5] In calculating these relationships it is assumed that the mass transfer of all species is diffusion controlled and that the diffusion coefficients of all species are the same.

Experimentally, electrooxidation of *o*-tolidine at pH 4.0 appears to follow the mechanism outlined; a stepped potential of +0.7 V *vs.* reference saturated calomel electrode produces a two-electron oxidation product. This product, designated at T, has an absorbance maximum at a wavelength of 437 mμ with a equal to 61,000 l. mole^{-1} cm^{-1}. The intermediate S absorbs at 365 and 630 mμ. The values of k_f tabulated in Table I are calculated from following the absorbance at wavelength of 437 mμ as a function of time during a 100-msec potential pulse.[6] The most consistent data analysis is obtained using the working curve for K_{eq} = 13 (25°). This equilibrium constant was evaluated by

Table I. Calculated Rate Constants

t, msec	A	$\pi^{1/2}A_T/[2a_T C_R^0\cdot(D_R t)^{1/2}]$	Log ($k_f t C_R^0$)	Log k_f	Recalcd log ($k_f t C_R^0$)
A. 6.0 × 10^{-4} *M* *o*-Tolidine in Acetate Buffer at pH 4.0					
10	0.0059[a]	0.74[b]	0.40	5.6	0.35
20	0.0078	0.69	0.59	5.5	0.65
30	0.0088	0.63	0.85	5.6	0.83
50	0.0096	0.56	1.23	5.7	1.05
80	0.0123	0.54	1.44	5.8	1.25
B. 2.0 × 10^{-3} *M* *o*-Tolidine in Acetate Buffer at pH 4.0					
10	0.0139	0.60	0.99	5.7	0.87
20	0.0192	0.58	1.12	5.5	1.17
30	0.0224	0.56	1.27	5.5	1.35
50	0.0277	0.53	1.56	5.6	1.57
80	0.0357	0.54	1.45	5.3	1.77
				Av 5.6 ± 0.1	
C. 5.0 × 10^{-4} *M* NN'DPP in Acetonitrile[c]					
10	0.00230[d]	0.50[e]	1.07[f]	6.37	
20	0.00365	0.57	1.44	6.44	
30	0.00465	0.59	1.57	6.39	
50	0.00625	0.60	1.70	6.30	
80	0.00815	0.62	1.92	6.32	
				Av 6.36 ± 0.04	

[a] Spectrally following species T, the diimine; molar absorptivity (a) = 6.1 × 10^4 l. mole^{-1} cm^{-1}. [b] Diffusion coefficient, D_R, of *o*-tolidine evaluated by following current–time during chronoamperometric experiments; $D^{1/2}$ = 1.95 × 10^{-3} cm sec$^{-1/2}$. [c] Supporting electrolyte is 0.3 *M* tetraethylammonium perchlorate. [d] Spectrally following species S, the free-radical intermediate; λ_{max} = 700 mμ; a = 1.1 × 10^4 l. mole^{-1} cm^{-1} in agreement with literature value (H. Linschitz, M. Ottolenghi, and R. Bensasson, *J. Am. Chem. Soc.*, **89**, 4592 (1967)). [e] K_{eq} > 200; diffusion coefficient of NN'DPP equals 1.66 × 10^{-5} cm^2 sec^{-1}.

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(3) Chronoamperometric experiment is one in which the potential is stepped to a value where the electrode reaction proceeds by diffusion control. Current-time relationship is described by the Cottrell equation; see P. Delahay, "New Instrumental Methods in Electrochemistry," Interscience Publishers, Inc., New York, N. Y., 1954.

(4) S. W. Feldberg and C. Auerbach, *Anal. Chem.*, **36**, 505 (1964).

(5) The normalized absorption of species S is simply related to that of species T by

$$\frac{\pi^{1/2}A_T}{2a_T C_R^0 (D_R t)^{1/2}} + \frac{1}{2}\,\frac{\pi^{1/2}A_S}{2a_S C_R^0 (D_R t)^{1/2}} = 1$$

(6) Depending on supporting electrolyte and concentration of *o*-tolidine, there is evidence of surface adsorption by *o*-tolidine. In acetate buffer, adsorption is minimized. Double potential step experiments with spectral monitoring have been performed to correct for adsorption effects. Details will be published shortly.

determining the equilibrium concentrations of species in bulk solution during coulometric experiments. It is in close agreement with cyclic voltammetry data.[7] The log $(k_f t C_R^0)$ and log k_f values (columns 4 and 5 of Table I) were calculated with this equilibrium constant. Using an average value of log $k_f = 5.6$, values of log $(k_f t C_R^0)$ were recalculated and then plotted *vs.* the normalized absorption parameter in Figure 1 to give an indication of the experimental precision of the method.

The oxidation of N,N′-diphenyl-*p*-phenylenediamine (NN′DPP) in acetonitrile follows the same reaction mechanism as *o*-tolidine. Data for this compound are also included in Table I.

The study of the wide variety of fast chemical reactions which follow charge transfer is now possible using these transparent electrodes. Theoretical analysis utilizing computer calculations has been completed for spectral determination of kinetic rates of a variety of reaction mechanisms following charge transfer. These analyses and the details of the associated experimental spectroelectrochemistry will be reported in the future.

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[7] Results do not preclude dimer formation by any of the species; calculations are in progress to evaluate dimer effects.

Jerzy W. Strojek, Theodore Kuwana
Department of Chemistry, Case Western Reserve University
Cleveland, Ohio

Stephen W. Feldberg
Brookhaven National Laboratory
Upton, New York

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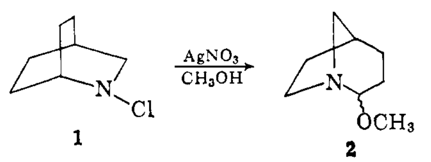
Internal Return in the Silver Ion Catalyzed Rearrangement of N-Chloramines

Sir:

The migration of alkyl groups to electron-deficient nitrogen has recently been shown to be a common occurrence in the rearrangement of bicyclic N-chloramines.[1] In view of the substantial increase in the rate of rearrangement in the presence of silver ion, it has been proposed that the reaction involves heterolysis of the nitrogen–chlorine bond. Thus, N-chloroisoquinuclidine (1) yields 60% of 2 when allowed to react with methanolic silver nitrate.[1]



1 2

While investigating the scope of this useful and mechanistically interesting alkyl migration to electron-deficient nitrogen, we prepared 4,7,7-trimethyl-2-chloro-2-azabicyclo[2.2.1]heptane[2] (3). When 3 was heated in methanol in a sealed tube at 70°, it had a half-life of 83 min.[3] When 3 (0.50 g) was added to 50 ml of a methanolic solution of silver perchlorate (1.0 g) at room temperature, it had a half-life of less than 1 min.[3] The presence of silver ion had resulted in a rate acceleration of at least 2×10^3. Undoubtedly, silver ion was intimately involved in the transition state for the reaction. *We wish to report that even though the silver ion plays a dominant role in the reaction of* **3**, *the major product contains chlorine.* Thus, 3 gave 77.5% of 4, 8.5% of 5, and 3.7% of 6.[4]

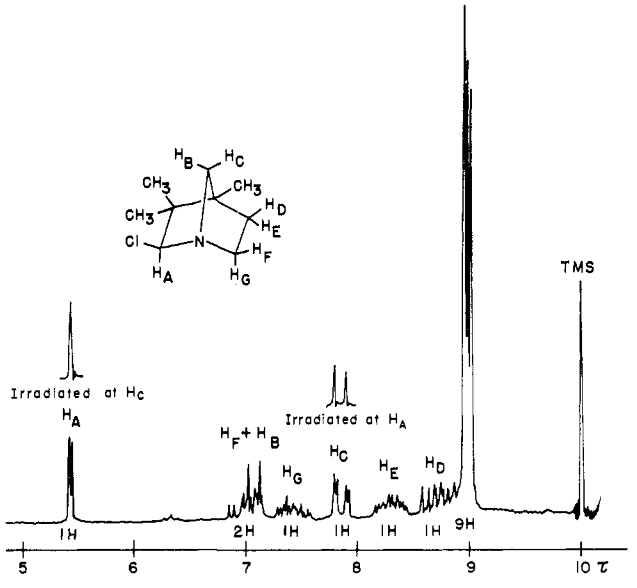
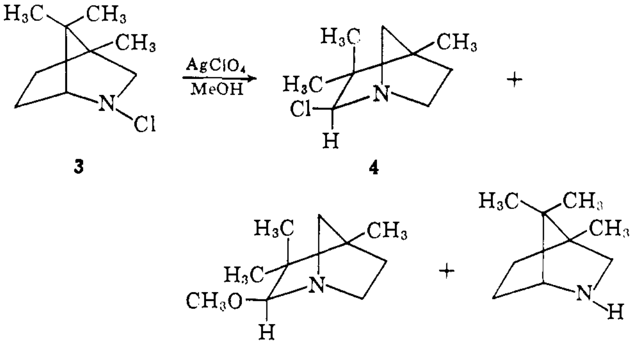


Figure 1.



3 4 5 6

The major product, 4, was analyzed for $C_9H_{16}NCl$. It contained no ionic or active chlorine. Thus, a carbon–chlorine bond must have been formed. On the basis of the nmr spectrum (100 Mc) shown in Figure 1, structure 4 was assigned to this chlorine-containing product. Of particular interest in this assignment was the doublet at τ 5.42 which was assigned to the hydrogen on the chlorine-bonded carbon. With $J_{AC} = 2.0$ cps it appeared that this hydrogen was coupled to the C-7-*anti* hydrogen which was assigned to the absorption at τ 7.85. This was proven by spin decoupling of these two signals, as shown in Figure 1. The C-7-*anti* hydrogen

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[1] P. G. Gassman and B. L. Fox, *J. Am. Chem. Soc.*, **89**, 338 (1967).

[2] The amine from which 3 is derived was synthesized from camphor in a seven-step sequence in 43% over-all yield. The details of this synthesis will be presented in a full paper on this work. Satisfactory elemental analyses have been obtained on all stable new compounds. The N-chloramines were not analyzed.

[3] Rates of reaction were measured by titrimetrically determining the amount of unreacted N-chloramine.

[4] We were not able to determine whether the small amount of 6 resulted from incomplete conversion of 6 into 3 or whether it arose from homolytic cleavage of the N-Cl bond of 3. In the absence of silver ion the relative yields of 4, 5, and 6 were 59, 20, and 7%, respectively.