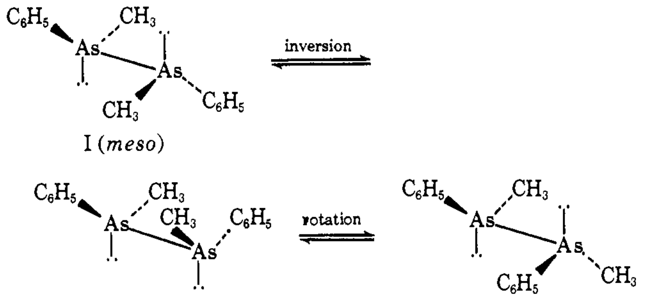
Horner, Campbell, and others[3] took advantage of this property in their successful resolutions of tertiary arsines. Moreover, all efforts by Horner to racemize the arsines by purely thermal means have failed.[4] Such an observation contrasts sharply with the properties of the analogous phosphines, which have a reported half-life for racemization of 3–5 hr at 130°.[5] In fact, racemization of (+)-methyl-*n*-propylphenylarsine could only be achieved in a first-order process by photolytic means.[6] In the Costain–Sutherland scheme used by Miller and coworkers,[7] the calculated inversion barrier for trimethylarsine is about 8–9 kcal/mole higher than that for trimethylphosphine.

In the present paper, we describe the first kinetic observation of the uncatalyzed, thermal stereomutation of arsenic. In order to circumvent the problems of configurational stability encountered by Horner in his work,[4] we have selected an appropriate diarsine for nmr studies. The diarsine system should invert much more rapidly than do simple arsines, because of more favorable p_π–d_π overlap in the transition state to inversion, in which half or all the molecule is planar, than in the ground state.[8] 1,2-Dimethyl-1,2-diphenyldiarsine[9] exists in *meso* (I) and *dl* (II) modifications, the stable *trans* forms of which are interconvertible by inversion of arsenic followed by bond rotation.[10] The nmr spectrum of this diarsine at 100° contains a multiplet from the phenyl protons at 6.5–7.2 ppm and two sharp peaks from the methyl protons in a ratio of 0.47:0.53 at 0.77 and 0.70 ppm below external TMS, the smaller peak being at lower field. Although ^{75}As (100% abundant) has a spin of $^3/_2$, coupling with adjacent protons is removed by the large quadrupolar interaction.[11] The two methyl peaks must therefore be due to the *meso* and the *dl* forms, respectively. Since the distance between the two peaks increases from 4.1 Hz at 60 MHz to 7.0 Hz at 100 MHz, the separation must be a chemical-shift difference rather than a coupling constant.



I (*meso*)

II (*dl*)

The two methyl peaks collapse to a clean singlet over the range 150–210° (T_c ~180° at 100 MHz). These spectral changes indicate the rapid interconversion of *meso*- and *dl*-1,2-dimethyl-1,2-diphenyldiarsine (I $\rightleftarrows$ II) by stereomutation of arsenic. The kinetics of the process were determined by a complete line-shape analysis.[12] The preliminary Arrhenius activation energy is 27 ± 3 kcal/mole.

Two alternative mechanisms may be excluded. A bimolecular inversion, in which two diarsine molecules exchange halves, requires that the rates be concentration dependent. The kinetics were found to be identical for 7 to 86% solutions by weight in biphenyl and only slightly different for a neat sample. Such an observation substantiates the unimolecularity of the reaction. It could also be argued that the two methyl peaks arise from different rotamers and that the observed rate process is therefore a rotation about the As–As bond. Tetramethyldiarsine (cacodyl) is capable of existing in several rotational conformations, but not in diastereomeric modifications. The observation by Harris and Hayter[11] that the nmr spectrum of cacodyl contains only one peak in the methyl region indicates that the rotamers indeed are conformationally averaged.

With the completion of the present work, unimolecular stereomutation by pyramidal inversion has now been observed for nitrogen,[13] oxygen,[14] phosphorus,[5a,b] sulfur,[15] and arsenic.

---

(3) L. Horner and H. Fuchs, *Tetrahedron Letters*, 203 (1962); I. G. M. Campbell and R. C. Poller, *J. Chem. Soc.*, 1195 (1956); M. S. Lesslie and E. E. Turner, *ibid.*, 1172 (1934).

(4) L. Horner and W. Hofer, *Tetrahedron Letters*, 3281 (1965).

(5) (a) L. Horner and H. Winkler, *ibid.*, 461 (1964); (b) for a comparison with diphosphines, see J. B. Lambert and D. C. Mueller, *J. Am. Chem. Soc.*, **88**, 3669 (1966).

(6) L. Horner and W. Hofer, *Tetrahedron Letters*, 3323 (1966).

(7) G. W. Koeppl, D. S. Sagatys, G. S. Krishnamurthy, and S. I. Miller, *J. Am. Chem. Soc.*, **89**, 3396 (1967).

(8) Many of the properties of diarsines are analogous to those of diphosphines, which have been reviewed recently by A. H. Cowley, *Chem. Rev.*, **65**, 617 (1965).

(9) J. W. B. Reesor and G. F. Wright, *J. Org. Chem.*, **22**, 382 (1957). The conjugating effects of the phenyl group may also serve to lower the barrier in this case.

(10) Spectral data point toward a preference for the *trans* rotamer; see ref 8 and (a) R. M. Lynden-Bell, *Trans. Faraday Soc.*, **57**, 888 (1961); (b) S. G. Frankies, *Spectrochim. Acta*, **23A**, 554 (1967); (c) E. G. Finer and R. K. Harris, *Mol. Phys.*, **12**, 457 (1967); (d) E. G. Finer and R. K. Harris, *ibid.*, **13**, 65 (1967).

(11) R. K. Harris and R. G. Hayter, *Can. J. Chem.*, **42**, 2282 (1964).

(12) J. B. Lambert, W. L. Oliver, and J. D. Roberts, *J. Am. Chem. Soc.*, **87**, 5085 (1965).

(13) For a review, see G. Binsch, "Topics in Stereochemistry," Vol. III, N. L. Allinger and E. L. Eliel, Ed., Interscience Publishers, Inc., New York, N. Y., in press.

(14) J. B. Lambert and D. H. Johnson, *J. Am. Chem. Soc.*, **90**, 1349 (1968).

(15) D. R. Rayner, E. G. Miller, P. Bickart, A. J. Gordon, and K. Mislow, *ibid.*, **88**, 3138 (1966); D. Darwish and G. Tourigny, *ibid.*, **88**, 4303 (1966).

(16) This work was supported by the National Science Foundation (Grant GP-6611).

(17) National Institutes of Health Predoctoral Fellow, 1966–1968.

(18) The authors are indebted to Dr. M. I. Levenberg and Mr. R. S. Egan of Abbott Laboratories, North Chicago, Ill., for the 100-MHz spectra.

Joseph B. Lambert,[16] George F. Jackson, III[17,18]
Department of Chemistry, Northwestern University
Evanston, Illinois 60201

Received December 26, 1967

Temperature Dependence of Product Composition in Reactions of Carbethoxynitrene with Anthracene and with Butene-2

Sir:

Reaction of carbethoxynitrene with polycyclic aromatic hydrocarbons yields a spectrum of products indicative of a dichotomy of mechanism.[1] Our suggestion that two different mechanistic pathways are initiated by attack on the substrate of the singlet and triplet forms of the nitrene[1] had sound analogy in reactions of 4-methylpentene-2[2] and was supported by a study of the concentration dependence of the isomer distribution of prod-

---

(1) A. L. J. Beckwith and J. W. Redmond, *Australian J. Chem.*, **19**, 1859 (1966).

(2) W. Lwowski and J. S. McConaghy, *J. Am. Chem. Soc.*, **87**, 5490 (1965).

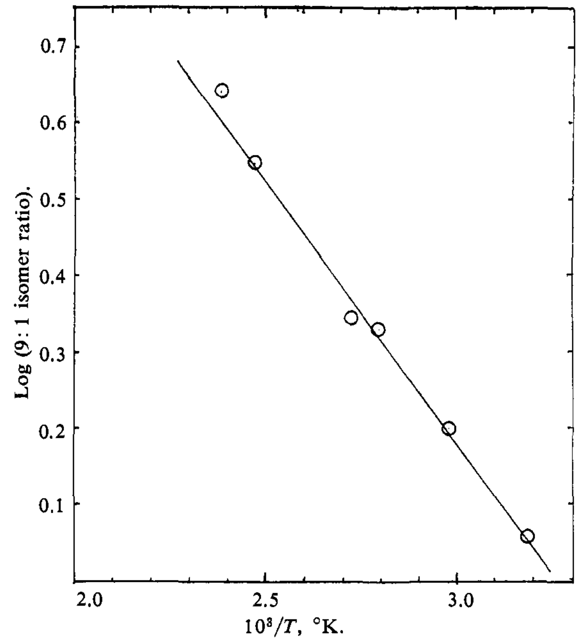


Figure 1. Temperature dependence of the 9:1 isomer ratio of anthrylurethans formed by the reaction of anthracene with carbethoxynitrene.

ucts from anthracene.[3] We have now determined the temperature dependence of the yields of products obtained by reaction of anthracene with carbethoxynitrene generated from N-*p*-nitrobenzenesulfonoxyurethan[4] by treatment with N,N-diethylcyclohexylamine.

Experimental conditions and results are summarized in Table I. The 9:1 isomer ratio of products increases with temperature, and there is a linear relationship between the logarithm of this ratio and $1/T$ (Figure 1). In terms of our mechanistic hypothesis, previously adumbrated,[3] that 9-anthrylurethan arises mainly from reaction of triplet carbethoxynitrene with anthracene, while the 1 isomer is formed by singlet attack, a plausible explanation for the present observations is that intersystem crossing in carbethoxynitrene is temperature dependent and has an apparent Arrhenius activation energy of approximately 3–4 kcal/mole greater than that for reaction of the singlet species at the 1,2 position.

Table I. Temperature Dependence of Yields of Urethans from the Reaction of Anthracene with Carbethoxynitrene[a]

		Urethan, %		9:1 isomer
Temp, °C	Solvent	1-Anthryl	9-Anthryl	ratio
40	CH_2Cl_2	15.0	17.1	1.13
61	$CHCl_3$	8.9	14.1	1.58
84	$ClCH_2CH_2Cl$	9.2	19.8	2.15
100	PhCl	9.0	19.8	2.20
132	PhCl	4.8	16.9.	2.52
147	$Cl_2CHCHCl_2$	4.2	16.2	3.9

[a] Reactant concentrations: anthracene = 0.95 mole %; N-*p*-nitrobenzenesulfonoxyurethan = 0.16 mole %; N,N-diethylcyclohexylamine = 0.16 mole %.

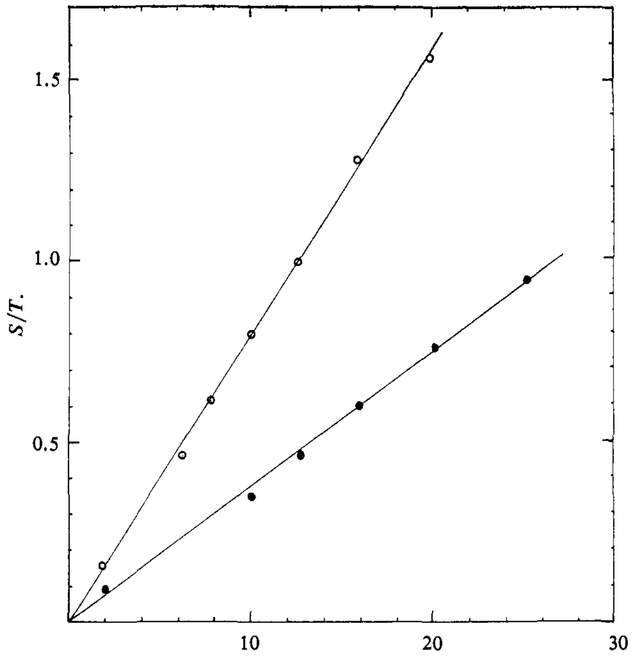


Figure 2. Ratio of products arising from singlet (S) and triplet (T) attack *vs.* olefin concentration for the reaction of *trans*-butene-2 with carbethoxynitrene at 80 (○) and 120° (●).

The use of the reaction with anthracene as a tool for probing the characteristics of intersystem crossing in carbethoxynitrene suffers from the disadvantages (i) that N,N-diethylcyclohexylamine appears to react preferentially with the triplet form[3] and (ii) that the singlet form may contribute to the observed formation of 9-anthrylurethan. Accordingly, further study was focused on the reactions of *cis*- and *trans*-butene-2 with carbethoxynitrene generated by thermolysis of ethyl azidoformate.[5]

Reactions were conducted in Freon TF solvent at 80 or 120° in sealed evacuated tubes and the resultant mixtures of *cis*- and *trans*-1-carbethoxy-2,3-dimethylaziridines, obtained in 60–70% absolute yield, were estimated by vpc. Each reaction was conducted at about ten different olefin concentrations (0.25–25 mole %) and the azide concentration was kept at [olefin]/15. The results were analyzed on the basis of Skell's hypothesis,[6] recently developed by Lwowski[2,7] and others,[8,9] that singlet species react stereospecifically with olefin while reactions of triplets are predominately nonstereospecific. The ratio of S, the amount of product arising from singlet attack, to T, the amount formed by triplet attack, is given by $S/T = X(x - 1)$ where x is the observed percentage of "wrong" isomer (*i.e.*, *cis*-aziridine from *trans*-olefin) in the product and X is the similar percentage arising solely by attack of the triplet species. It follows from Scheme I that X represents the precentage of wrong isomer obtained at infinite dilution and that $S/T = k_2[\text{olefin}]/k_1$. Consequently a plot of S/T *vs.*

---

(3) A. L. J. Beckwith and J. W. Redmond, *Chem. Commun.*, 165 (1967).

(4) W. Lwowski and T. J. Maricich, *J. Am. Chem. Soc.*, **87**, 3630 (1965).

(5) M. F. Sloan, T. J. Prosser, N. R. Newburg, and D. S. Breslow, *Tetrahedron Letters*, 2945 (1964); R. J. Cotter and W. F. Beach, *J. Org. Chem.*, **29**, 751 (1964); R. Kreher and D. Kuehling, *Angew. Chem.*, 77, 42 (1965); W. Lwowski and T. W. Mattingly, *J. Am. Chem. Soc.*, **87**, 1947 (1965).

(6) P. S. Skell and R. C. Woodworth, *ibid.*, **78**, 4496 (1956).

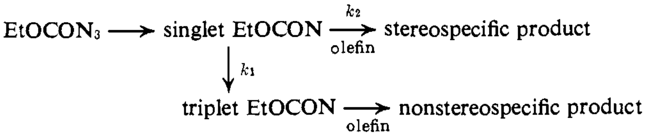
(7) J. S. McConaghy and W. Lwowski, *ibid.*, **89**, 2357 (1967).

(8) K. Hafner, W. Kaiser, and R. Puttner, *Tetrahedron Letters*, 3593 (1964); M. Jones and K. R. Rettig, *J. Am. Chem. Soc.*, **87**, 4013, 4015 (1965); E. Ciganek, *ibid.*, **88**, 1979 (1966).

(9) R. F. W. Bader and J. I. Generosa, *Can. J. Chem.*, **43**, 1631 (1965).

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

Scheme I



$$\mathrm{EtOCON_3} \longrightarrow \text{singlet EtOCON} \xrightarrow[\text{olefin}]{k_2} \text{stereospecific product}$$
$$\downarrow k_1$$
$$\text{triplet EtOCON} \xrightarrow[\text{olefin}]{} \text{nonstereospecific product}$$

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.

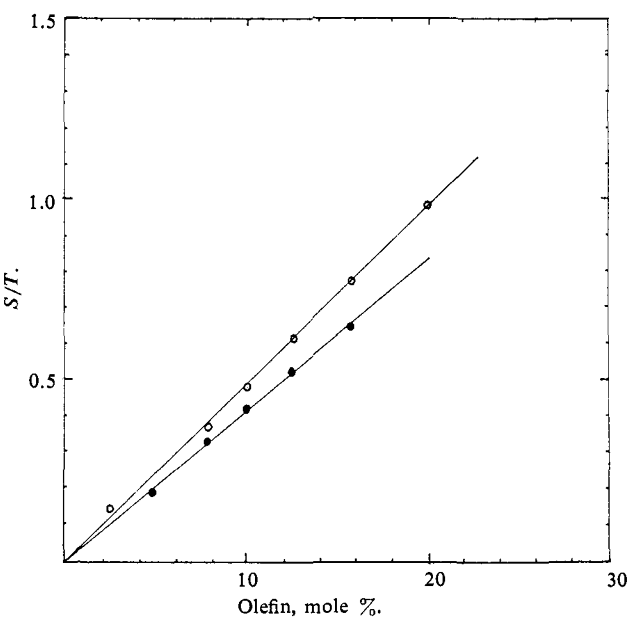


Figure 3. Ratio of products arising from singlet (S) and triplet (T) attack *vs.* olefin concentration for the reaction of *cis*-butene-2 with carbethoxynitrene at 80 (○) and 120° (●).

---

(10) J. S. McConaghy and W. Lwowski, *J. Am. Chem. Soc.*, **89**, 4450 (1967).

(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]

(12) For a recent review see S. K. Lower and M. A. El-Sayed, *Chem. Rev.*, 66, 199 (1966).

(13) J. B. Birks and I. H. Munro, *Progr. Reaction Kinetics*, **4**, 239 (1967).

(14) A. G. Anastassiou, *J. Am. Chem. Soc.*, **88**, 2322 (1966).

(15) A. N. Strachan and D. E. Thornton, *J. Phys. Chem.*, 70, 952 (1966).

(16) P. J. Wagner, *J. Chem. Phys.*, **45**, 2335 (1966).

(17) J. B. Birks, C. L. Braga, and M. D. Lumb, *Proc. Roy. Soc.* (London), **A283**, 83 (1965).

(18) E. C. Lim, J. D. Laposa, and J. M. H. Yu, *J. Mol. Spectry.*, **19**, 412 (1966).

(19) R. C. Henson and E. D. Owen, *Chem. Commun.*, 153 (1967).

(20) K. A. Muszkat, D. Gegiou, and E. Fischer, *J. Am. Chem. Soc.*, **89**, 4814 (1967).

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

(22) N. C. Baird and M. J. S. Dewar, *ibid.*, **89**, 3966 (1967).

A. L. J. Beckwith, J. W. Redmond
Organic Chemistry Department, University of Adelaide
Adelaide, South Australia 5000
Received November 13, 1967

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.

---

(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).