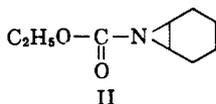
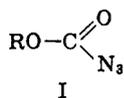


COMMUNICATIONS TO THE EDITOR

FLASH-PHOTOLYTIC DECOMPOSITION OF GASEOUS ALKYL AZIDOFORMATES

Sir:

We have studied the flash-photolytic decomposition of gaseous methyl and ethyl azidoformates, I. We have identified the principal, ultraviolet-absorbing transient



decomposition product of both compounds with flash ultraviolet absorption spectra. We have collected and identified the main product of the flash-photolytically-induced reaction of gaseous ethyl azidoformate, with cyclohexene vapor. The evidence from this work points firmly to the existence of a highly reactive and unstable nitrene of the form RO-CO-N.

Recent work has demonstrated that the photodecomposition of ethyl azidoformate in liquid cyclohexene leads to the formation, in good yield, of the aziridine II, 7-carbomethoxy-7-azabicyclo[1.4.0]heptane.¹ This reaction and the photolytic decomposition of I in liquid cyclohexane leading to cyclohexylurethane¹ point strongly to the presence of a nitrene intermediate. The work reported here was undertaken to study the possible existence of a gaseous nitrene, and to investigate rapid reactions of such a species.

Photolysis and spectroscopy were carried out with apparatus differing only slightly from that reported previously.² A multiple-pass sample cell (path length up to 3.2 m.) was used for many of the spectra, a McPherson 2.217-m. grating spectrograph was used for the spectra from which the wave length measurements were made and a rotating-drum camera mounted behind medium quartz and glass spectrographs was used for some of the time-dependence measurements. Spectra were taken at times from 12 $\mu\text{sec.}$ to several minutes after initiation of photolysis. Photolyses were carried out with partial pressures of azidoformate of 8 to 15 mm. and with the added inert gases CO₂, N₂ and Ar. The most effective condition for producing the principal transient absorber were *p*(azidoformate) 8–9 mm. and *p*(CO₂) 300 mm. Nitrogen and argon were less efficient than CO₂ as stabilizing media. In the absence of inert gas, the transient was detected, but only with difficulty.

The principal transient absorber is the radical NCO. This is unequivocally identified by a comparison of our spectra with those reported by Dixon.³ We observe both the ²II–²II and ²Σ⁺–²II transitions. In the band system of the former, we have found the bands at 315.0, 314.8, 305.1, 304.5, 296.4, 295.9 and 294.8 mμ and in the latter, the bands at 440.3, 438.9, 438.4, 435.1, 435.0, 434.8, 416.7, 415.0, 413.7, 413.3, 399.3 and 397.7.

The NCO radical is detectable at times as short as 12 $\mu\text{sec.}$ after initiation of photolysis of either azidoformate. The intensity of the bands reaches a maximum at about 20 $\mu\text{sec.}$, at which time the photolysis lamp is

(1) W. Lwowski and T. W. Mattingly, *Tetrahedron Letters*, 277 (1962).

(2) R. S. Berry, G. N. Spokes and M. Stiles, *J. Am. Chem. Soc.*, **84**, 3570 (1962).

(3) R. N. Dixon, *Can. J. Phys.*, **38**, 10 (1960); *Phil. Trans. Roy. Soc. (London)*, **262**, 165 (1959); R. Holland, D. W. G. Style, R. N. Dixon and D. A. Ramsay, *Nature*, **182**, 336 (1958).

still intense, but is decaying. The intensity of NCO absorption is greater when the methyl compound is the source than when the ethyl compound is used. The half-life of NCO is about 200 $\mu\text{sec.}$ with the methyl precursor, and about 50 $\mu\text{sec.}$ with the ethyl. Intensity measurements as functions of time, made under the optimum conditions described above, indicate that the disappearance of NCO follows kinetics which are first order in the NCO concentration. If one adds NO at any partial pressure down to 15 mm., the NCO bands are not observed. When cyclohexene vapor is present at pressures of 20 mm. or more, the bands are not detected; if the cyclohexene pressure is as low as 0.3 mm., the NCO bands are weak but detectable.

From the photolysis of ethyl azidoformate in the presence of 20 mm. of cyclohexene, the aziridine (II) was isolated by vapor chromatography and identified by comparison of its retention time and infrared spectrum with an authentic sample prepared previously.¹ (The column was silicone, at 150°.)

We conclude that I loses N₂ to give an unstable and reactive nitrene RO-CO-N. This may be trapped if a suitable substrate is present; otherwise its C–O single bond breaks. The formation of NCO by attack of the nitrene on the alkyl group, followed by decomposition of a cyclic intermediate, is unlikely, because of the higher photolysis yield of NCO from the methyl compound than from the ethyl.

The transient spectra also show bands in the region of 2700 Å. which we have not identified, and which are now being investigated.

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**A NOTE ON STERIC ISOTOPE EFFECTS.
CONFORMATIONAL KINETIC ISOTOPE EFFECTS IN THE
RACEMIZATION OF 9,10-DIHYDRO-4,5-
DIMETHYLPHENANTHRENE**

Sir:

The smaller amplitude of vibration of deuterium as compared to that of protium is reflected in a smaller van der Waals radius.¹ In a recent attempt to assess the importance of this factor in kinetics,² we concluded that highly crowded transition states would be required for the exhibition of secondary isotope effects arising from differences in non-bonded repulsions of the isotopes, *i.e.*, steric isotope effects. This requirement is eminently satisfied in the racemization of 9,10-dihydro-4,5-dimethylphenanthrene (I)³: in the transition state for racemization the extreme congestion of the two methyls, acting as classical blocking groups, results in molecular deformations which must be largely responsible for the observed activation energy barrier of 23 kcal./

(1) *E.g.*, A. R. Ubbelohde, *Trans. Faraday Soc.*, **32**, 525 (1936).

(2) K. Mislow, R. E. O'Brien and H. Schaefer, *J. Am. Chem. Soc.*, **82**, 5512 (1960); **84**, 1940 (1962), and references cited therein.

(3) K. Mislow and H. B. Hopps, *ibid.*, **84**, 3018 (1962).