

ment to a CN stretching vibration which is somewhat coupled to vibrations of other parts of the molecule. Although the 868 cm^{-1} peak cannot be attributed to a pure out-of-plane wagging motion of a CH_2 group, the observed isotopic substitution dependence of this peak could be rationalized in terms of the expected mixing of this vibration with the out-of-plane bending fundamental of the CCN chain. The appearance of this absorption at a frequency significantly higher than that of the out-of-plane deformation fundamental of CH_3 [9, 10] is not inconsistent with such an assignment, in view of the expected interaction of the unpaired electron of CH_2CN with the π electrons on the CN group. The closely related H_2CF free radical has also recently been observed in this laboratory to photodecompose on exposure of the sample to the full light of a medium-pressure mercury arc.

In summary, H atom detachment has been found to predominate both on 1216 \AA photolysis of CH_3CN isolated in an argon matrix and on collisional interaction of CH_3CN with $11.5 - 11.7\text{ eV}$ excited argon atoms, followed by the trapping of the products in solid argon at 14 K . Secondary photodecomposition processes play a much more important role in the 1216 \AA photolysis studies than in the excited argon atom studies. A major product in the excited argon atom studies is ketenimine, $\text{CH}_2=\text{C}=\text{NH}$, previously identified in matrix isolation studies of the reaction of NH with C_2H_2 . A partial vibrational assignment for ketenimine is possible, utilizing the detailed isotopic data obtained in these experiments. A band system between 3060 and 2500 \AA may also be contributed by ketenimine. Present data permit only a tentative identification of CH_2CN .

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







PHOTOCHEMICAL REACTIONS OF NITROMETHANE IN NON-AQUEOUS SOLUTIONS

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Investigations on photochemical properties of nitromethane have been carried out for many years and have been mainly concerned with the photolysis of nitromethane in the gaseous and liquid phases and in frozen matrices [1, 2]. The dissociation of the C—N bond into free radicals CH_3 and NO_2 has been assumed as the most probable primary process of nitromethane photolysis. This abstract presents results of photochemical studies on nitromethane in benzene, cyclohexane and isopropanol solutions irradiated with wavelengths of 254 nm , longer than 290 nm and 313 nm . Nitroalkanes show two absorption bands at about 200 nm and 270 nm . However, we have shown after a precise examination of the nitromethane spectrum that an additional band at 330 nm can be

TABLE 1

Cyclohexane			Isopropanol	Benzene	
254 nm	313 nm	$\Phi \times 10^4$	254 nm	313 nm	$\Phi \times 10^5$
 NO ₂	—	—	(CH ₃ NO) ₂	 OCH ₃	30
 ONO ₂	+	33	(CH ₃) ₂ CO	 NO ₂	68
 NO ₂	+	~0,6	(CH ₃) ₂ C=NOH	 OH NO ₂	29
 NOH	+	4	(CH ₃) ₂ CN ₂ NOCH ₃ OH	 OH	15
 O	+	24	(CH ₃) ₂ CHONO	 OH	~8
 OH	+	8	CH ₃ ONO	 O ₂ N—OH	—
CH ₃ ONO	+	—	CH ₃ ONO	 CH ₃	—
					(trace)

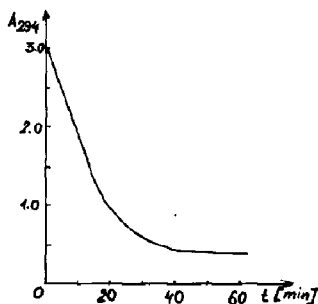
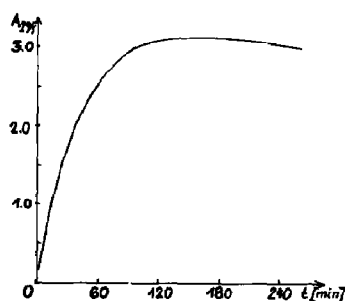


Fig. 1. Nitrosodimer formation in the nitromethane–cyclohexane system irradiated with $\lambda = 254$ nm and measured at 294 nm ($c_0 = 0.14$ M, $l = 0.1$ cm).

Fig. 2. Nitrosodimer decomposition in the nitromethane–cyclohexane system irradiated at a photostationary state with $\lambda > 290$ nm and measured at 294 nm.

observed. The identified photoproducts and some of their quantum yields of formation at 313 nm in degassed solutions are reported in Table 1.

All products were determined by means of UV, IR, vapour phase chromatography and mass spectrometry techniques. Preliminary photokinetic studies of cyclohexylo-nitrosodimer formation in the nitromethane–cyclohexane system have been performed and are presented in Figs. 1 and 2.

Similar results of the disappearance of an authentic sample of nitrosodimer in cyclohexane solution upon irradiation have been obtained. The essential role of nitrosodimer formation and decomposition on the formation of photoproducts in the nitromethane–cyclohexane system has been emphasized. The plausible mechanisms of most of the products formed in aprotic and protic solvents under investigation have been discussed and postulated. The results of our work point to a significant role of the primary photochemical reaction of CH₃NO₂ leading to free radical (CH₃ and NO₂) splitting in the photochemistry of nitromethane in non-aqueous solutions (hydrogen abstraction, and photosubstitution reactions [3]). However, the influence of excited CH₃NO₂* molecules on the formation of photoproducts in isopropanol and cyclohexane solutions cannot be ruled out.

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CORRELATED EXCITATIONS IN CONJUGATED MOLECULES

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The discovery of the forbidden 2^1A_g state below the 1^1B_u state in polyenes and diphenylpolyenes [1, 2] has revived the photochemistry of these molecules. The 2^1A_g state is to be described as a concerted excitation of two B_u triplet states forming a covalent singlet spin wave in the polyene π system [2]. The low energy position of this state and its remarkable physical properties rationalize the photoactivity of polyenes. Spectroscopic work carried out in recent years has revealed the exact energy position of the 2^1A_g state relative to the 1^1B_u state in a series of polyenes and their derivatives. However, the observations were at variance with the early theoretical description [2] which has extended a PPP-CI treatment to include all double excitations in order to account for the triplet-triplet character of these states. We demonstrate now that these states also exhibit long range spin coupling of a quadruplet-quadruplet and quintet-quintet type extending over several adjacent ethylene units. This character must be accounted for by triple and quadruple excitations in a CI treatment to achieve the proper behaviour of the 2^1A_g - 1^1B_u energy gap, an increase in going from butadiene (where the 2^1A_g actually lies above the 1^1B_u level) to decapentaene and a saturation from thereon [3].

Recently the idea has emerged that the *cis-trans* photoisomerisation of stilbene is governed by a higher excited 1A_g state which exhibits a minimum at the perpendicular conformation crossing the lowest excited 1B_u state upon bond rotation. An evaluation of the potential surfaces governing the photoisomerisation process (by a PPP-SCF-CI method) revealed that there indeed exists such a photochemically active 1A_g state which in the planar molecule lies about 1 eV above the lowest absorption band and involves the excitation of two electrons from the ground state [4]. Extensions of the calculations to the diphenylpolyenes demonstrate that this 1A_g state is related to the one-photon forbidden low lying triplet-triplet spin wave state of the polyenes [4]. Such a state is predicted to be photochemically active also in the visual chromophore (a protonated Schiff base of retinal) very much the same way as in stilbene.

The question arises how far covalent spin wave excitations extend in conjugated molecules. We have carried out a study of the polyazene spectra and have established that such states also exist in large numbers in these molecules. On the basis of extended PPP-SCF-CI calculations we predict energy level schemes which consistently account for the spectral data available and, in addition, contain some one-photon forbidden transitions yet unobserved [3].

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