

Molecular Photochemistry. VIII. Evidence for a Singlet-State Complex in the Photocycloaddition of Acetone to *trans*-1,2-Dicyanoethylene^{1,2}

Sir:

Photocycloaddition of the n, π^* triplet state of ketones to electron-rich olefins appears to be a general primary photochemical process.³⁻⁶ We have presented evidence that the photocyclization of acetone to the electronic-deficient substrate *trans*-dicyanoethylene (*t*-DCE) does not proceed *via* the acetone triplet.⁷ We now wish to

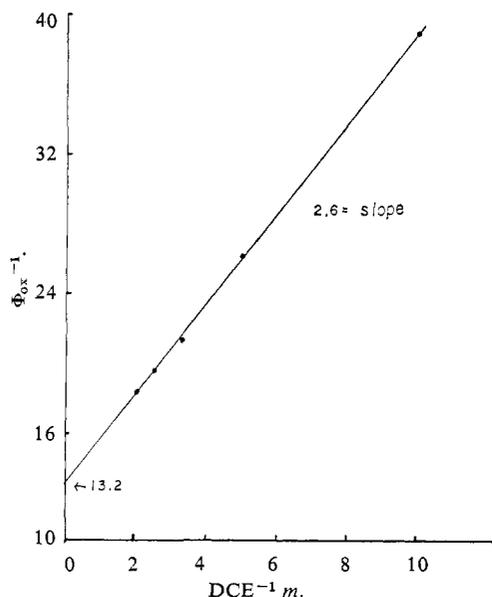
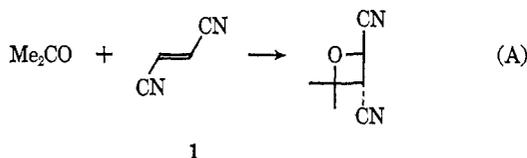


Figure 1. Plot of [quantum yield of *trans*-oxetane formation]⁻¹ against [*trans*-DCE]⁻¹.

present evidence that photocycloaddition of acetone to *t*-DCE does not proceed *via* the n, π^* singlet state of acetone but rather *via* a singlet complex of acetone and *t*-DCE. Furthermore, it appears that the side reaction of isomerization of *t*-DCE to *cis*-DCE involves a different excited state of acetone, probably the triplet.



The quenching of acetone-sensitized *t*-DCE → *c*-DCE isomerization by varying amounts of 1,3-pentadiene (a quencher known to deactivate acetone triplets at the diffusion-controlled rate)^{8b} results in typical Stern-

(1) The authors gratefully acknowledge the generous support of this work by the Air Force Office of Scientific Research (Grants AFOSR-1000-66 and AFOSR-1380-68) and the National Science Foundation (Grant NSF-GP-4280).

(2) Part VII: N. J. Turro and R. Engel, *J. Am. Chem. Soc.*, **90**, 2989 (1968).

(3) Reviews: D. R. Arnold, *Advan. Photochem.*, in press; L. L. Muller and J. Hamer, "1,2-Cycloaddition Reactions," Interscience Publishers, Inc., New York, N. Y., 1967, p 111.

(4) N. C. Yang, M. Nussim, M. J. Jorgenson, and S. Murov, *Tetrahedron Letters*, 3657 (1964).

(5) D. R. Arnold, R. L. Hinman, and A. H. Glick, *ibid.*, 1425 (1964).

(6) L. A. Singer and G. A. Davis, *J. Am. Chem. Soc.*, **89**, 598 (1967).

(7) N. J. Turro, P. Wriede, J. C. Dalton, D. Arnold, and A. Glick, *ibid.*, **89**, 3950 (1967).

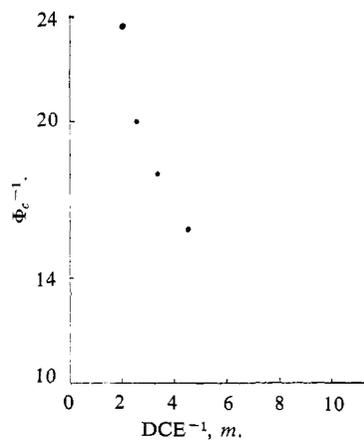


Figure 2. Plot of [quantum yield of *cis*-DCE formation]⁻¹ against [*trans*-DCE]⁻¹.

Volmer behavior. The slope of this plot is 2 for [*t*-DCE] = 0.5 M, indicating that *t*-DCE and 1,3-pentadiene are equally effective in quenching the precursor of *c*-DCE.⁸ Under identical conditions the photocycloaddition of acetone and *t*-DCE to form the oxetane **1** is not quenched by 1,3-pentadiene.

A Stern-Volmer analysis of oxetane formation is shown in Figure 1. The slope of this plot is about 3, but the intercept is close to 13.

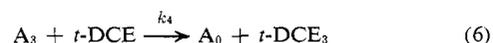
Finally, Figure 2 shows the effect of *t*-DCE concentration of Φ_{c-DCE} . At high concentrations of *t*-DCE the formation of *c*-DCE is strongly quenched, a result which demands that different precursors exist for the production of oxetane and *c*-DCE.

The usual kinetic analysis of reaction A may be represented by the Stern-Volmer relationship, where a = the efficiency of formation of the chemically active species in oxetane formation.

$$\frac{1}{\Phi_{ox}} = \frac{1}{a} + \frac{k_{st}}{ak_1[t-DCE]}$$

$$a = \frac{k_2}{k_2 + k_3}$$

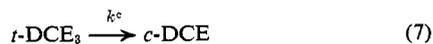
The mechanism given by eq 1-9 explains these results most economically.¹⁰



(8) (a) The triplet excitation energy of *t*-DCE is not known. However, maleic anhydride possesses $E_T \sim 72$ kcal/mol: W. M. Hardham and G. S. Hammond, *J. Am. Chem. Soc.*, **89**, 3200 (1967). It is not unreasonable, therefore, to assume that *t*-DCE possesses $E_T < 78$ kcal/mol, the triplet energy of acetone.⁹ (b) P. J. Wagner, *J. Am. Chem. Soc.*, **89**, 2503 (1967).

(9) R. F. Borkman and D. R. Kearns, *ibid.*, **88**, 3467 (1966).

(10) Steps 3, 4, and 5 could also involve direct addition of A_1 to *t*-DCE in competition with complex formation of A_1 and *t*-DCE to produce $A_0 + t-DCE$. There is no way of distinguishing the two processes, but it is not unlikely that addition and complexation are related.



Since the intercept of Figure 1 is much larger than one, steps 3, 4, and 5 are included in order to provide a path for formation of oxetane which does not involve singlet acetone as the chemically active species.

Using the values of $1/a = 13.2$ and $k_{st}/ak_1 = 2.6$, a value of $k_1/k_{st} = 5$ is obtained. The same ratio is available from a Stern-Volmer analysis of the quenching of acetone fluorescence by *t*-DCE, which also gave a value of ~ 5 ; *i.e.*, the latter result implies that the major mode of quenching acetone fluorescence is complex formation.^{11,12}

(11) L. A. Singer and G. A. Davis, *J. Am. Chem. Soc.*, **89**, 158 (1967), have described the cycloaddition reaction of fluorenone and ketenimines which is quenched by addition of high concentrations of ketenimine.

(12) For other recent examples of singlet quenching see L. M. Stephenson, D. G. Whitten, G. F. Vesley, and G. S. Hammond, *ibid.*, **88**, 3665 (1966); H. E. Zimmerman and J. S. Swenton, *ibid.*, **89**, 906 (1967); S. D. Andrews and A. C. Day, *Chem. Commun.*, 477 (1967).

(13) Fellow of the Alfred P. Sloan Foundation.

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Refined Molecular Structure of the Heptamolybdate and Hexamolybdotellurate Ions¹

Sir:

As part of a continuing program intended to provide detailed information concerning the molecular structures of the class of inorganic oxo compounds of V, Nb, Ta, Mo, and W known as the heteropoly and isopoly complexes, the methods of three-dimensional X-ray diffraction have now been applied to two polymolybdate compounds. The two new crystal structure studies have revealed the details of the structures of the heptamolybdate ion $[\text{Mo}_7\text{O}_{24}]^{6-}$ and the hexamolybdotellurate ion $[\text{TeMo}_6\text{O}_{24}]^{6-}$. The salient chemical results of these studies are reported here, but the details of the associated crystal structure analyses will be published in another place.

In 1950 Lindqvist² reported his study of the crystal structure of ammonium heptamolybdate (paramolybdate), $(\text{NH}_4)_6[\text{Mo}_7\text{O}_{24}] \cdot 4\text{H}_2\text{O}$, in which he determined the locations of seven independent Mo atoms in the crystal. Lindqvist did not resolve the oxygen atoms, but he proposed the most probable configuration of the whole complex ion on the basis of reasonable, assumed Mo-O distances and octahedral edge sharing. The unit-cell parameters of the crystal were originally reported by Sturdivant³ as follows: monoclinic with $a = 8.399 \text{ \AA}$, $b = 36.198 \text{ \AA}$, $c = 10.485 \text{ \AA}$, $\beta = 116^\circ 0'$; space group $P2_1/c$ ($Z = 4$). For this compound 8200 independent reflection data were collected by visual estimate of intensities on multiple-film Weissenberg patterns made with Mo $K\alpha$ radiation. In a full-

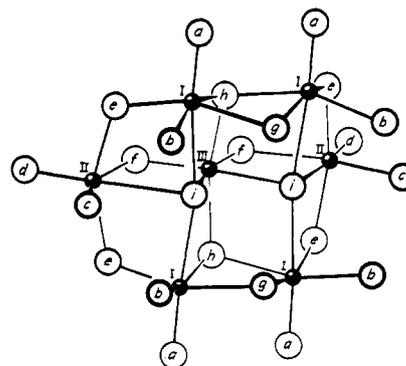


Figure 1. Oblique view of the heptamolybdate molecule ion $[\text{Mo}_7\text{O}_{24}]^{6-}$. Atoms are labeled according to the ideal 2mm symmetry (a horizontal mirror plane contains Mo_{II} , Mo_{III} , O_e , O_d , O_f and O_i ; a vertical mirror plane contains Mo_{III} , O_g , and O_h , and a two-fold axis lies at their intersection).

matrix, least-squares analysis of these data, 176 parameters were varied, leading to a reliability factor of $R = 0.096$. The initial model was derived from a three-dimensional electron density synthesis, for which the Fourier phases were found from a structure-factor computation based only on the Mo atom positions as given by Lindqvist. The electron density map revealed all the atoms in the structure except hydrogen atoms, and the least-squares refinement converged rapidly in a completely straightforward way. Lindqvist's proposal for the configuration was fully confirmed. The heptamolybdate molecule ion has no symmetry that is required by the crystal symmetry, but conforms closely to the point-group symmetry 2mm (C_{2v}), which presumably is that assumed by the free ion in solution. The complex ion is shown in Figure 1 with the different types of atoms labeled. The averaged bond lengths and the maximum variation of the individual bond lengths in the crystal (which are determined with a standard error of 0.01 \AA) are listed in Table I.

Table I. Bond Lengths in the Heptamolybdate Complex Ion $[\text{Mo}_7\text{O}_{24}]^{6-}$, Averaged over the Ideal Molecular Symmetry 2mm (see Figure 1)

Bonded atoms	No. of bonds in molecule	Max var in crystal, \AA	Av bond length, \AA
$\text{Mo}_{\text{I}}\text{-O}_a$	4	0.015	1.710
O_b	4	0.028	1.728
O_e	4	0.027	1.966
O_g	4	0.034	1.945
O_h	4	0.012	2.179
$\text{Mo}_{\text{II}}\text{-O}_c$	2	0.008	1.716
O_d	2	0.012	1.741
O_e	4	0.018	1.915
O_f	2	0.078	2.415
O_i	2	0.010	2.155
$\text{Mo}_{\text{III}}\text{-O}_f$	2	0.007	1.754
O_h	2	0.012	1.903
O_i	2	0.006	2.264
$\text{Mo}_{\text{I}}\text{-Mo}_{\text{I}}$	2	0.015	3.257
$\text{Mo}_{\text{I}}\text{-Mo}_{\text{II}}$	4	0.031	3.206
$\text{Mo}_{\text{I}}\text{-Mo}_{\text{III}}$	4	0.029	3.405
$\text{Mo}_{\text{II}}\text{-Mo}_{\text{III}}$	2	0.048	3.434

In 1948 a brief note⁴ was published describing the results of a preliminary study of the hexamolybdotellurate complex ion as contained in the orthorhombic

(4) H. T. Evans, Jr., *ibid.*, **70**, 1291 (1948).

(1) Publication approved by the Director, U. S. Geological Survey.

(2) I. Lindqvist, *Arkiv Kemi*, **2**, 325 (1950).

(3) J. H. Sturdivant, *J. Am. Chem. Soc.*, **59**, 630 (1937).