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NOTES

Room-Temperature Colored Transients in Ozonolysis of Aryl Olefins and Acetylenes on Silica Gel

The mechanism of ozonolysis of unsaturated compounds in solution is currently an active field of investigation (*1*). A number of transients have been detected in the case of olefins at low temperature and these have been identified as π complexes, molozonides, and/or zwitterions (*1b*).

We have recently described ozonolysis of crystalline aryl olefins (stilbene, tetraphenylethylene, stilboestrol) and of tolane with particular emphasis on the effect of crystal structure and imperfections on the observed reaction characteristics (*2*). Continuing these studies on microcrystals of several related compounds, we noticed that two electron-donor substituted derivatives, namely, tetraanisylethylene (TAE) and bis-paramethoxytolane (DMT), after exposure to an ozone stream at room temperature for approximately 10 min, displayed a weak pink color; this color slowly faded as the ozonolysis proceeded. As the reaction is fast in solution (CH_2Cl_2, cyclohexane) and no color is perceived, we believed that, in crystals, a donor–ozone complex is stabilized in the reaction cavity (*3*). In order to trap these presumably ionic intermediates we have carried out the reactions on the preceding aryl olefins and acetylenes adsorbed on silica gel (*4*). We wish to report on the observation of stable colored transients obtained for the first time under these conditions and on their tentative assignment.

The compounds in Table 1 (≈30 mg) were adsorbed on silica gel (500 mg) (commercial silica gel, Kieselgel, 70–230 mesh ASTM, Merck, heated in an electric furnace at 350°C for 24 hr and stored at 225°C). A stream of ozone (≈2–3% O_3 in O_2) was blown at room temperature onto the surface of the powder in a dry atmosphere for variable periods of time. Products were extracted with organic solvents (such as acetone, alcohol and acetic acid) and were characterized by thin-layer chromatography and spectroscopic methods with reference to authentic samples. In the case of tolanes, overall chemical yields did not exceed 10%, most of the (unidentified) products remaining bound to the silica. Results are reported in Table 1.

With three compounds, we observed a red-purple (or pink) coloration immediately at the beginning of the flow of ozone. The color disappeared after about 30 min (TAE) or 10–15 min (MMT and DMT). Electronic spectra (Figs. 1 and 2) were recorded by the reflectance technique described in Ref. (*5*). ESR spectra were recorded on a Varian V 4500 spectrometer. ATR experiments were carried out according to Ref. (*6*).

Olefins

Colored species obtained by flushing olefins with O_3 have already been detected by Bailey *et al.* (*1b*) at low temperature.

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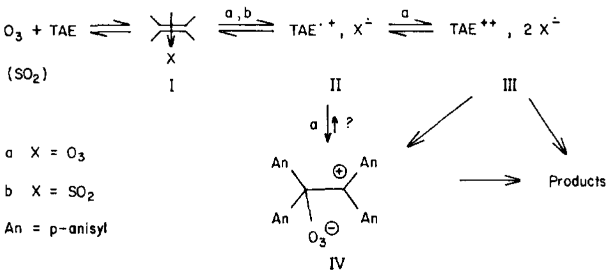
These have been ascribed to π-complexes as the absorption maximum is red-shifted with increasing number of donor substituents.

We will first discuss tetraanisylethylene. This compound seems to be able to give a complex with O_3; moreover, it is known to generate the radical–cation $TAE^{\cdot+}$ in CH_2Cl_2 and the dication TAE^{++} (*7*) in CH_3CN. The uv spectra of these species are known and do not fit with the ones we observed. However, electronic spectra may be strongly affected when compounds are adsorbed on silica gel (*8*). The radical–cation of the parent compound, tetraphenylethylene (TPE), in polycrystalline CCl_4 at −196°C exhibits a single maximum (*9*) near 500 nm (Fig. 1, curve 5); for $TAE^{\cdot+}$ adsorbed on silica gel, we must expect a bathochromic shift and the spectrum we obtained (Fig. 1, curve 1) might therefore be ascribed to this intermediate. Moreover, we were able to observe an ESR signal ($g = 2.003$, singlet, total width ≈ 3.1 mT) for the red species the intensity of which decreased very rapidly with time. The signal may be assigned (*10*) to the radical–cation $TAE^{\cdot+}$. *The same signal* was observed (*11*) when O_3 was replaced by the isoelectronic compound SO_2. With SO_2, TAE formed a yellow species.

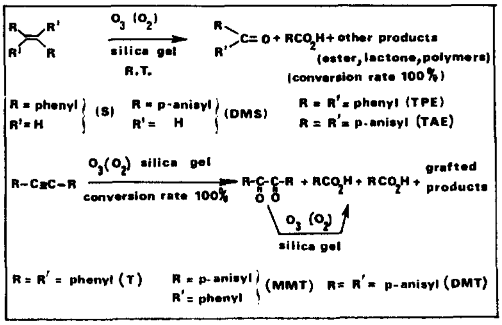
In both cases, no ESR signal was detected respectively for $O_3^{\cdot-}$ and $SO_2^{\cdot-}$ which would be less stable than $TAE^{\cdot+}$, probably in part because of the acidity of silica gel. Bailey *et al.* (*12*) recorded the ESR spectrum of the red $O_3^{\cdot-}$ produced at −90°C with amines in CH_2Cl_2, but even at the same temperature when t-$BuNH_2$ was adsorbed on silica gel we could detect only a pale green coloration. Only unadsorbed (liquid) t-$BuNH_2$ showed an orange coloration under those conditions. We produced red $O_3^{\cdot-}$ by blowing O_3 onto KOH pellets and recorded the reflectance uv spectrum which showed a broad structureless band with $\lambda_{max} \approx 450$ nm (*13*).

The following scheme, in agreement with the foregoing results, is proposed as a working hypothesis.



The red color cannot be ascribed with precision but it may be due to several transients; radical–cation $TAE^{\cdot+}$ and zwitterion (IV) (*14*) are equally probable candidates. Attempts to characterize these species by resonance Raman and attenuated total reflection (ir) met with failure. In addition, we will note that TAE is nearly all recovered after the action of SO_2; the latter has a lower electron affinity than O_3 and we believe that the yellow color is ascribable to π-complex (I), whereas only

TABLE 1



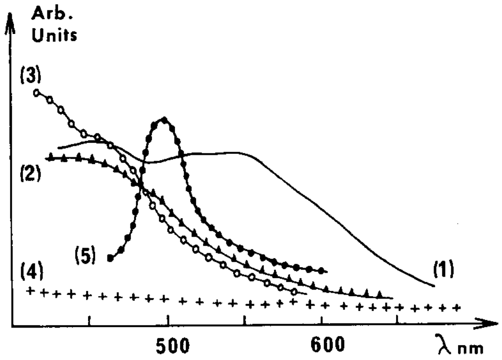


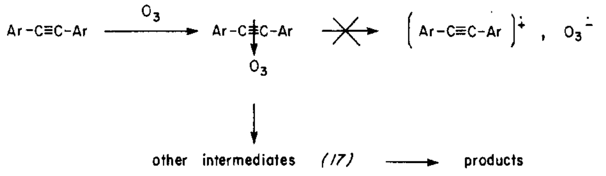
FIG. 1. Absorption electronic spectra of: (1) TAE/silica gel + ozone after a few minutes; (2) TAE/silica gel + ozone after 30 min; (3) TAE/silica gel + SO_2; (4) TAE/silica gel before reaction; (5) $TPE^{\cdot +}$ in polycrystalline CCl_4 (−196°C).

traces of $TAE^{\cdot +}$ might be formed (ESR is more sensitive than uv).

None of the other olefins gave a color with O_3 despite the fact that they were completely converted into products, probably because their ionization potential is not low enough (*15*) to produce electron transfer.

Tolanes

Methoxylated tolanes give pink transients (Fig. 2) which show maxima at about the same wavelengths as in the case of TAE. However, these do not exhibit any ESR signal (under our conditions). As tolanes are poorer reducing agents than olefins (*15*), it is likely that electron transfer does not occur. It is to be noted that by cyclic voltammetry on DMT in CH_2Cl_2 + $(CF_3CO)_2$ + CF_3CO_2H, no evidence was found for the stability of the initial oxidation products, i.e., cation–radical or dication (*16*). Consequently, the colored species might be assigned to π-complexes (scheme below).



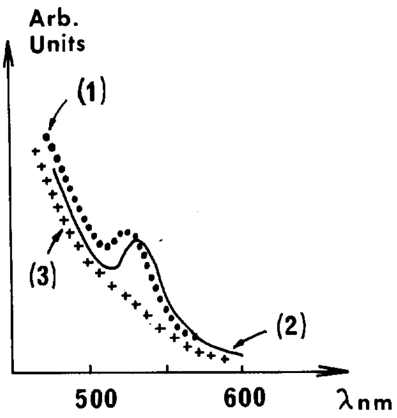


FIG. 2. Absorption electronic spectra of: (1) MMT/silica gel + ozone after a few minutes; (2) DMT/silica gel + ozone after a few minutes; (3) MMT or DMT/silica gel + ozone after 15 min.

One should ask, then, why *p*-dimethoxystilbene (DMS) does not exhibit, under these conditions, similar colored π-complexes. This is probably because of their greater reactivity, the lifetime of these complexes being shortened as they immediately collapse into other colorless intermediates.

The greatest parts of the products were not recovered by extraction with organic solvents and are believed to be grafted at the surface of the adsorbent as silicon derivatives.

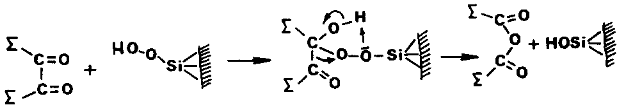
Interestingly, benzil was smoothly converted into benzoic acid which was quantitatively isolated under our conditions. In pentane solution at 20 or −78°C, benzil was recovered. In the usual oxidation of α-diketones into carboxylic acids (*18*), H_2O_2, peracids or KO_2 is used.

We now wish to clarify the role of silica as catalyst in the above reactions. In contrast to the crystalline state, the adsorbed molecules exhibit, under exposure to ozone, strong colorations which are due to radical–cations, dications, or charge transfer species. The colorations appear as soon as the flushing of ozone begins, so the concentration of the gas itself may not be held responsible for these effects; on other adsorbents, for example, alumina, no coloration has been detected. Hence we argue that it is not merely a surface effect.

Moreover, if the organic crystals are transformed to oxidized products very slowly, the adsorbates are particularly sensitive to oxidation and a marked decrease (or even a total disappearance) in the initial coloration is observed during the reaction. So the behavior of molecules adsorbed onto silica gel is quite different from that of the molecules forming crystals. The adsorbent probably modifies at least the initial stages of the reaction by facilitating electron transfer and stabilizing the polarized species which are formed.

Indeed, on one hand, Weis *et al.* (*19*) have shown, by recording ultraviolet absorption spectra of benzene, naphthalene, myrcene, etc., that silica gel does favor the formation of ionic species and stabilizes them; on the other hand, Porter and Hall (*20*) and Rooney and Pink (*21*) have demonstrated that anthracene, 1,1′-diphenylethylene, etc., adsorbed on a mixture of silica/alumina, readily give radical ions and carbocations. In the latter case, oxidation would be due to the Lewis acid sites of alumina.

That the adsorbent must also play a major role in the subsequent steps of the reaction is exemplified by the case of α-diketones which, while very stable in the crystalline state, are easily transformed when adsorbed on silica gel. It is reasonable to assume that —Si–OH groups are oxidized into peroxisilanes with O_3, in which case the acid formation may be schematized as follows.



We may also suppose that α-diketones, on silica, are slightly more polarized than free molecules; thus addition of O_3 should be facilitated.

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REFERENCES

1. (a) Bailey, P. S., *Chem. Rev.* **58**, 925 (1958); Criegee, R., *Angew. Chem. Int. Ed. Engl.* **14**, 745 (1975). (b) Bailey, P. S., Ward, J. W., Carter, T. P., Jr., Nieh, E., Fisher, C. M., and Khashab, A. I. Y., *J. Amer. Chem. Soc.* **96**, 6136 (1974) and references therein. (c) Alcock, W. G., and Mill, B., *J. Chem. Soc. Chem. Commun.* **5** (1976) and references therein.

2. Bouas-Laurent, H., Desvergne, J. P., Lapouyade, R., and Thomas, J. M., *Mol. Cryst. Liq. Cryst.* **32**, 143 (1976) and references therein.

3. Cohen, M. D., *Angew. Chem. Int. Ed. Engl.* **14**, 386 (1975).

4. (a) Burwell, R. L., *Chem. Technol.* **4**, 370 (1974). (b) Cohen, Z., Keinan, E., Mazur, Y., and Varkony, T. H., *J. Org. Chem.* **40**, 2141 (1975).

5. Surles, T., Erickson, J. O., and Priesner, D., *Int. Lab.*, May/June 29 (1975).

6. Szymanski, H. A. (Ed.), "Raman Spectroscopy, Theory and Practice." Plenum Press, New York, 1967.

7. Svanholm, U., Jensen, B. S., and Parker, V. D., *J. Chem. Soc. Perkin Trans.* **2**, 907 (1974) and references therein.

8. Leermakers, P. A., Thomas, H. T., Weis, L. D., and James, F. C., *J. Amer. Chem. Soc.* **88**, 5075 (1966).

9. Kaiser, E. T., and Kevan, L. (Eds.), "Radical Ions," p. 321. Wiley, New York, 1968.

10. Fischer, H., *in* Landolt-Börnstein, "Numerical data and functional relationships in Science and Technology," New series, (K. H. Hellwege, ed.), Group II, Atomic and Molecular Physics Vol. 1: magnetic properties of free radicals. Springer-Verlag, Berlin, 1965.

11. Nojima, M., Nagao, G., Kakeya, N., Takagi, M., and Tokura, N., *J. Chem. Soc. Chem. Commun.* 486 (1976).

12. Bailey, P. S., Keller, J. E., and Carter, T. P., *J. Org. Chem.* **35**, 2777 (1970).

13. Salomon, I. J., Kacmarek, A. J. McDonough, J. M., and Hattori, K., *J. Amer. Chem. Soc.* **82**, 5640 (1960).

14. Photoelectric Spectrometry Group, England, and Institut fuer Spektrochemie and Angewandte Spektroskopie, Germany, "UV Atlas of Organic Compounds," Vol. 1, Plenum Press, New York, 1966.

15. (a) Watanabe, K., Nakayama, T., and Mottl, J., *J. Quant. Spectrosc. Radiat. Transfer* **2**, 369 (1962). (b) Gutman, F., and Lyons, L. E., "Organic Semiconductors." Wiley, New York, 1967.

16. Parker, V. D., personal communication.

17. De More, W. B., and Lin, C. L., *J. Org. Chem.* **38**, 985 (1973).

18. (a) Leffler, J. E., *J. Org. Chem.* **16**, 1785 (1951). (b) San Filippo, J., Chern, C. I., and Valentine, J. S., *J. Org. Chem.* **41**, 1078 (1976).

19. Weis, L. D., Evans, T. R., and Leermakers, P. A., *J. Amer. Chem. Soc.* **90**, 6109 (1968).

20. (a) Porter, R. P., and Hall, W. K., *J. Catal.* **5**, 336 (1966). (b) Hall, W. K., *J. Catal.* **1**, 53 (1962).

21. Rooney, J. J., and Pink, R. C., *Trans. Faraday Soc.* **58**, 1632 (1962).

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