Do Ozone–Olefin Complexes Really Exist?

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Abstract: The interaction between ozone and simple olefins in argon, carbon dioxide, and nitrogen matrices has been studied by UV and IR absorption spectroscopy. No evidence for ozone–olefin complexes was obtained. Previous claims of ozone–olefin complexes were based on observations made at temperatures where ozone reacts rapidly with olefins.

Introduction

The complex formation between ozone and carbon π electron systems has been the subject of a few investigations. Bailey et al.[1-3] observed absorption bands from a reversible interaction between ozone and several aromatic substrates. The probable site of interaction is the aromatic system or in the case of mesitylphenylethylene possibly a conjugated styrene system. Hull et al.[4] also observed a UV absorption band at 385 nm for the toluene–ozone system at temperatures around 110 K. Both for this system and for a number of ozone–olefin systems (also at 110 K) they observed an ozone-like IR absorption which they interpreted as evidence for ozone–olefin complex formation. In ozonolysis of 2,4,4-trimethylpent-1-ene at 91 K Alcock and Mile[5] observed a red-brown coloration and two IR bands which they assigned to the ν_2 and ν_3 bands of complexed ozone.

We have earlier reported[6] a study of the ethylene–ozone interaction in carbon dioxide and carbon tetrachloride matrices. At a temperature between 65 and 77 K they react to form 1,2,4-trioxolane and one other compound, possibly[4,6] 1,2,3-trioxolane. Using the same technique we have now studied the interaction between ozone and propylene, *cis*- and *trans*-2-butene, tetramethylethylene, and benzene in carbon dioxide matrices at temperatures above 65 K by means of UV and IR spectroscopy.

We have also investigated the ozone–ethylene, and ozone–benzene, and ozone–tetramethylethylene systems in nitrogen and argon matrices at temperatures below 40 K.

Experimental Section

Apparatus and Procedure. The carbon dioxide matrix experiments were carried out in a liquid nitrogen cooled cryostat equipped with cesium iodide windows. The temperature of the cold window (measured with a platinum resistance thermometer) could be kept constant anywhere between 65 K and room temperature to within a few hundredths of a degree.[7] The carbon dioxide matrices were deposited at 65 K at a rate of 1.5–2 mmol/h.[8] Deposition time was 3.5–6.5 h.

For the argon and nitrogen matrix work two cryostats were used: a He cryostat which has been described earlier[9,10] and a cryostat using an Air Products CS 208 refrigeration system with window and thermometer arrangements similar to the He cryostat.

The deposition system has been described earlier.[8] The deposition rate was ca. 1.6 mmol/h. The deposition temperature was 20 K for nitrogen matrices and 10.9 K for argon matrices, except when otherwise stated. Deposition time was 3–19 h.

All infrared spectra were run on a Perkin-Elmer 180 instrument which was calibrated with standard gases.[11]

In the course of this work, the spectrometer was connected to an LSI Alpha minicomputer (32K) with a Pertec disk and a Houston DP 1 plotter. This system will be described later.[12]

All UV spectra were recorded on a Cary 15-M spectrometer.

Chemicals. Carbon dioxide (L'Air Liquide 99.995%) was used without further purification.

Nitrogen and argon (L'Air Liquide 99.9995%) were passed through a glass spiral immersed in $N_2(l)$ or $O_2(l)$, respectively.

Benzene (Fisher B245) was purified by fractional crystallization and distillation on a vacuum line.

Tetramethylethylene (Fluka 98%) was purified by gas chromatography on a Perkin-Elmer F21 preparative gas chromatograph with 20% dinonylphthalate in Chromosorb columns.

Ethylene (L'Air Liquide 99.95%), propylene (Matheson 99%), and *cis*- and *trans*-2-butene (both L'Air Liquide 99%) were all used without further purification.

Ozone was prepared by a tesla coil discharge through oxygen of low pressure in a closed system cooled with liquid nitrogen. Residual oxygen was removed by pumping at 77 K.

Gas mixtures were prepared using standard manometric techniques. The ozone/substrate/matrix ratio was 1:1:100 in the argon and nitrogen matrices and varied between 1:1:30 and 1:1:100 in the carbon dioxide matrices.

Results and Discussion

When benzene and ozone are codeposited in a carbon dioxide matrix a UV absorption with a maximum at 354 nm is obtained indicating the formation of a charge-transfer complex between benzene and ozone. Warmup from 65 to 90 K does not affect this absorption significantly. With propylene and *cis*- and *trans*-2-butene a reaction has occurred already during deposition at 65 K, giving as major products a 1,2,4-trioxolane and another product, probably the corresponding 1,2,3-trioxolane.[4] Tetramethylethylene also reacts to products which cannot possibly be identified as a tetramethylethylene–ozone complex (see Figure 1). Ethylene reacts during warmup from 65 to 77 K.

With benzene and ozone in an argon matrix deposited at 10.9 K or in a nitrogen matrix at 20 K the CT–UV absorption is obtained with a maximum at 350 nm. We also observe a broadening of the ν_4 IR band of benzene in the argon matrix, probably due to a benzene–ozone complex. However, when benzene–ozone are deposited in nitrogen at 10.9 K the 350-nm band is barely detectable. In the 12–20 K interval, an increase of the temperature by 1 K leads to a slow increase of the 350-nm absorption maximum which appears to level off after about 1 h. A new temperature increase then leads to a new absorption increase, etc. In the 20–26 K region no significant increase is observed, while above 27 K the absorption slowly grows, probably due to bulk diffusion.

For the ethylene–ozone system in argon and nitrogen the IR spectra are superpositions of ozone and olefin spectra. In the tetramethylethylene case (deposition temperature 20 K) in addition to the starting materials a set of new, relatively weak bands are observed. When the temperature is increased to 35–40 K for ca. 10 min and then lowered back to 20 K most of these peaks grow. Their positions make it impossible to interpret them as ozone complex peaks. In fact their positions are close to the peaks observed in the carbon dioxide matrix (see Figure 1). (Even for a weak complex the C=C stretching vibration should be IR active, which it is not.)

UV spectra were run down to where the olefin absorption made further observations impossible (approximately 180 nm for ethylene and 210 nm for tetramethylethylene). No absorption that can be assigned to anything but ozone or olefin was found.

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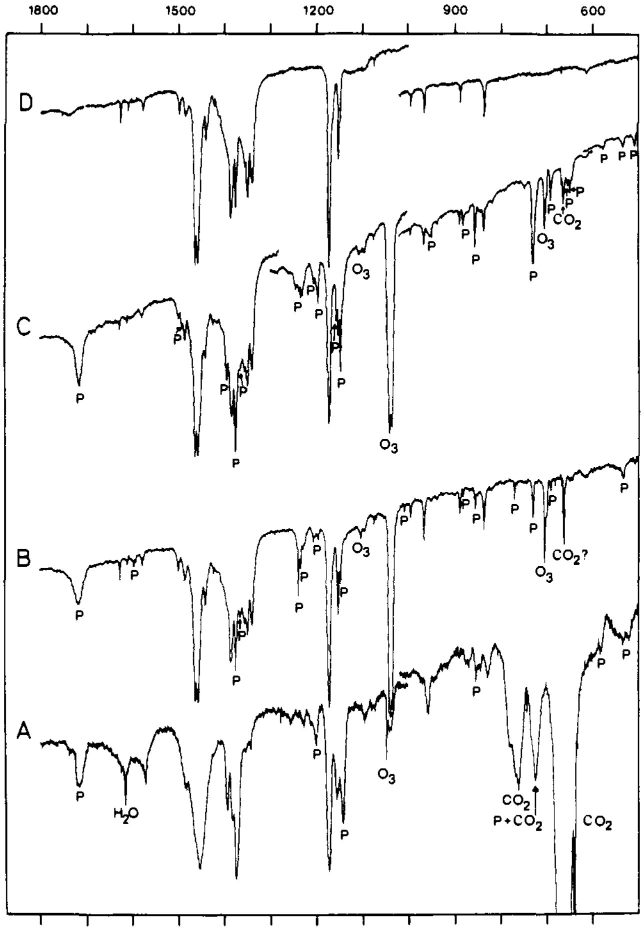

Figure 1. IR spectra of the tetramethylethylene-ozone system. (A) $(CH_3)_2C{=}C(CH_3)_2{:}O_3{:}CO_2$ (1:1:100), 77 K after deposition at 65 K, 9 mmol deposited. (B) $(CH_3)_2C{=}C(CH_3)_2{:}O_3{:}Ar$ (1:1:100), 20 K immediately after deposition, 28 mmol deposited. (C) Same experiment as B, 20 K after about 10 min at 35-40 K. (D) $(CH_3)_2C{=}C(CH_3)_2{:}Ar$ (1:100), 20 K immediately after deposition, 24 mmol deposited. P, product of reaction.

Empirical data for a large number of charge-transfer complexes show that for a given electron acceptor the position of the charge-transfer band is essentially determined by the ionization potential of the donor.[13] Therefore, reasonable estimates of ozone-olefin CT band positions can be made from the UV data of Bailey et al.[3] and our observation of the benzene-ozone CT band. For ethylene we obtain 265 ± 50 nm and for tetramethylethylene 455 ± 40 nm. While there is a possibility that an ethylene-ozone charge transfer band is hidden under the strong ozone UV band, there is no measurable absorption at all at longer wavelengths than the ozone band in the tetramethylethylene case.

The curious behavior of the benzene-ozone complex in nitrogen and the rather small shift of the benzene ν_4 IR band indicate that the benzene-ozone complex is rather weak. The very large shifts of the ozone bands for the postulated 2,4,4-trimethylpent-1-ene-ozone complex[5] would indicate the surprising result that this complex is very strong.

Earlier reports[4,5] of ozone-olefin complexes are based on observations at temperatures above 90 K while our experiments show that (with the exception of ethylene) reaction (not complex formation) occurs below 65 K. Hull et al.[4] deposited ozone and olefin on separate layers, on top of each other. It therefore seems probable that their reaction temperatures are determined by the diffusion rate of ozone in the mixed olefin-reaction product phase rather than applicable to solid, homogeneous ozone-olefin mixtures[14] or isolated pairs of ozone and olefin molecules. We therefore favor the alternative explanation of Hull et al. that their ozone IR absorptions are due to dissolved ozone (probably in the reaction product phase).

In order to observe olefin-ozone complexes one probably has to work at temperatures below 40 K. The absence of a charge-transfer band for the tetramethylethylene-ozone system in solid argon indicates that the interaction between this olefin and ozone is not significantly stronger than the argon-ozone or argon-olefin interactions.

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References and Notes

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(14) When argon matrices containing ethylene and ozone were warmed to evaporate the argon, a blue solid formed, which exploded violently upon further warming. With benzene-ozone or just ozone in the matrix no explosions occurred.