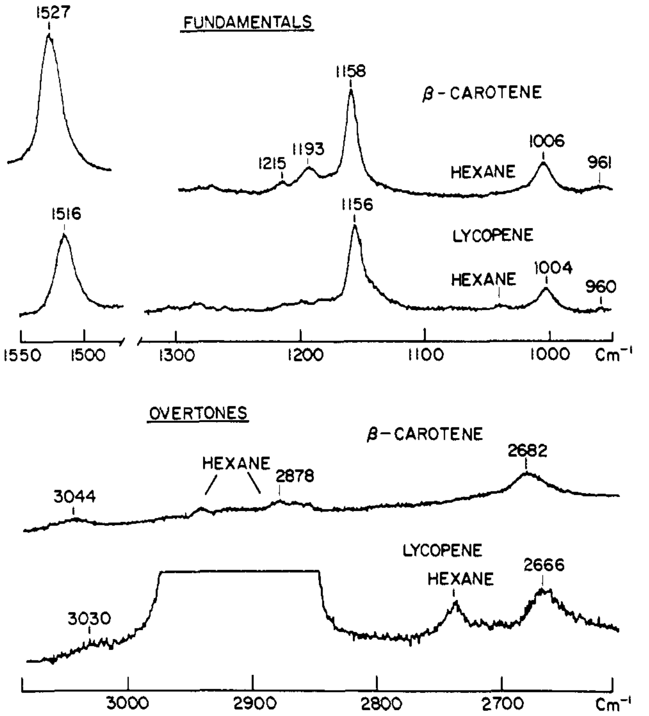

Figure 1. Example of resonance-enhanced Raman (RR) spectra of carotenoid solutions in *n*-hexane taken in a reflection geometry: [β-carotene] 100, [lyocpene] 4.5 μM; argon laser excitation at 488 nm for β-carotene and 514.5 nm for lycopene; laser power ~100 mW; incident and analyzed scattered E field perpendicular to scattering plane; Jarrell-Ash 75-cm Czerny-Turner double grating monochromator, photon counting digital detector; integration time ~1 sec; scanning rate 20 cm^{-1}/min.

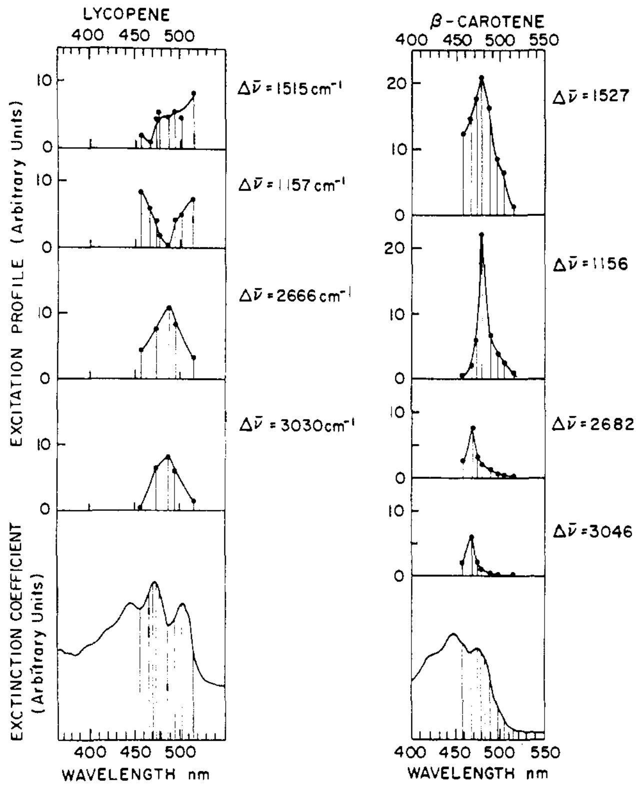

Figure 2. Excitation profiles of several fundamental and overtone lines in the RR spectra of β-carotene and lycopene in *n*-hexane solutions. Solvent Raman lines were used as internal standards. Vertical lines emphasize the eight monochromatic emissions of the argon laser used for excitation. Fundamentals at $\Delta\bar{\nu} < 1600$ cm^{-1}; the rest are overtones. Corresponding sections of the absorption spectra are shown at the lower part.

from any of the absorption peaks. In lycopene, we observe a peak at λ ~490 in the overtone EP, and the slope of the fundamental EP indicates the presence of a peak at a wavelength much longer than the first absorption peak.

In lycopene, we have a clear indication that the frequency of the 0–0 transition $\bar{\nu}_{00}$ is lower than that of the lowest electronic absorption peak at $\bar{\nu}$ 19,802 cm^{-1} (λ 505 nm), since the slope of the excitation profile for Raman fundamentals shows the presence of at least one peak below this frequency. Such may also be the case of β-carotene and of many other polyenes.[29] Although the vibrational fundamentals are very similar in both our samples, the vibronic splittings in the absorption spectra are different. If we assume that the vibrational frequencies in the excited state are close to those of the ground state,[27] we conclude that whereas in β-carotene the vibronic splitting (1240-cm^{-1} separation between the first two absorption maxima) corresponds to ν_1, in lycopene it is ν_2 (1566-cm^{-1} separations between absorption peaks). If, by analogy, we further assume that in carotene the $\bar{\nu}_{00} + n\bar{\nu}_1$ states contribute to the EP of the Raman fundamentals and the $\bar{\nu}_{00} + m\bar{\nu}_2$ states contribute to the EP of overtones (with the reverse perhaps true for lycopene), we can assign the difference between the two peaks of the two EP's of β-carotene to $(2\bar{\nu}_1 - \bar{\nu}_2) \simeq 740$ cm^{-1}, thus predicting for the excited state $\bar{\nu}_2 \sim 1500$ cm^{-1}. Such a scheme would also predict two more EP peaks, at $\bar{\nu}_{00}$ and at $\bar{\nu}_{00} + 1120$, both within the range of our experiments, and which we have not observed. This, however, could be expected, since generally different vibronic sublevels in the excited state are expected to contribute differently to the EP.[10,30–32]

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Acknowledgment. We acknowledge helpful discussions with Mrs. M. H. Heyde and Mr. J. L. Parsons.

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Mechanistic Aspects of the Reaction of Acids with Some Platinum–Acetylene Complexes

Sir:

The oxidative addition reaction of a number of protonic acids to low-valent platinum complexes has been studied by a number of workers.[1–4] We have

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(1) F. Cariati, R. Ugo, and F. Bonati, *Inorg. Chem.*, 5, 1128 (1966).

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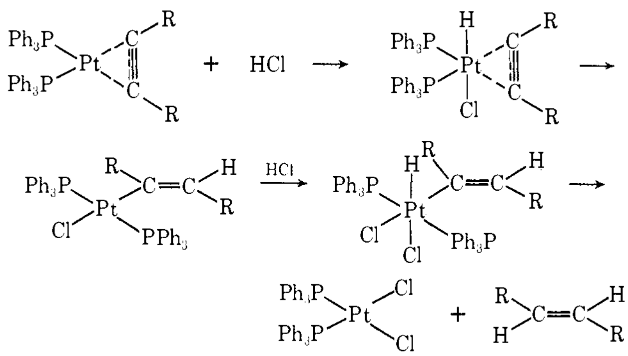
(4) I. Harvie and R. D. W. Kemmitt, *ibid.*, 198 (1970). The unusual reaction of $(PPh_3)_4Pt$ with aldehydes described in this publication gives complexes of stoichiometry $Pt(COEt)_2(PPh_3)_2$ and $Pt(COPh_3)_2(PPh_3)_2$. The reported infrared spectra of these complexes are identical, however, with $Pt(COOEt)_2(PPh_3)_2$ and $Pt(COOPh)_2(PPh_3)_2$ prepared from $Pt(CO_3)(PPh_3)_2$ and the corresponding acids, and it is very likely that the reported complexes are the dicarboxylates rather than the diacyls.

found that strong acids (HX) will readily add to the complexes $(PPh_3)_2Pt$(acetylene) to give $(PPh_3)_2PtX_2$,[5] with the hydrogen transferring to the acetylene to form an olefin. The reaction proceeds with the initial formation of a vinyl complex which may then react further with a second molecule of the acid to give the olefin. Most of our work has been carried out with HCl, but the reaction also proceeds with HBr, picric acid, thioacetic acid, and trifluoroacetic acid,[6] all of which have been found to give hydrides with $(PPh_3)_4Pt$.[5]

We have found that the reaction with the but-2-yne complex is very rapid with a quantitative conversion to but-2-ene; gas chromatography shows that the isomers are in the thermodynamic ratio of 80% *trans* and 20% *cis*, and that there is no formation of alkane. The diphenylacetylene complex reacts with HCl in $CHCl_3$ solution to give a quantitative yield of *trans*-stilbene, but in benzene solution the yield is only about 60%. *cis*-$(PPh_3)_2PtCl_2$, which is obtained in quantitative yield with the but-2-yne complex and with the diphenylacetylene complex in $CHCl_3$ as solvent, is insoluble in common organic solvents, but the nonvolatile residue from the reaction of the diphenylacetylene complex in benzene as solvent is however partially soluble in $CHCl_3$. The nmr spectrum of this complex in $CDCl_3$ shows a multiplet for the phenyl protons at τ 2.75 and a sharp singlet at τ 3.13. This resonance can be assigned to the protons in the vinyl complex by analogy with other platinum vinyl complexes.[6,7] When HCl is added to this solution the peak at τ 3.13 disappears and is replaced by a peak at τ 3.01, which is identical in position with the nmr of the olefinic proton in pure stilbene (mp 122°) as prepared by us, and by comparison with the published value.[8] Final confirmation of the structure of the complex has been obtained by preparing it by the addition of only 1 mol of HCl to the diphenylacetylene complex.[9] From this reaction the vinyl complex has been obtained pure (*Anal.* Calcd for $C_{50}H_{41}P_2ClPt$: C, 64.20; H, 4.38; Cl, 3.78. Found: C, 64.14; H, 4.29; Cl, 4.01) and shows a band in the ir for the C=C stretch at 1590 cm^{-1} (m) and the nmr peak for the olefinic protons at τ 3.13.

We believe that the mechanism of the reaction is the one shown in Scheme I, which involves the intermediate formation of two platinum hydrides. A study has been made of the replacement reaction of one acetylene coordinated to $(PPh_3)_2Pt$ by a second acetylene, and the mechanism has been considered to follow a scheme where dissociation to $(PPh_3)_2Pt$ occurs initially followed by the reaction of this reactive intermediate with the second acetylene to form the new complex.[10] It is possible that a similar mechanism may occur in this reaction, where the acetylene initially dissociates to give $(PPh_3)_2Pt$ which then oxidatively adds HCl to give the hydride.[1] The free acetylene can then insert into the platinum hydride to give the intermediate vinyl complex. Although this second mechanism is possible, we favor the one proposed since we have been unable to readily insert diphenylacetylene into $(PPh_3)_2$-Pt(H)Cl to give the vinyl complex even under the acid conditions prevailing in the reaction. We have not isolated either of the intermediate hydrides but they represent reasonable structures since hydrides of both Pt(II)[1,2,11] and Pt(IV)[1,12] have been isolated and characterized in similar systems. With $(PPh_3)_2Pt$-$(CF_3C{\equiv}CCF_3)$ and excess HCl the product is the vinyl complex $(PPh_3)_2Pt(Cl)[(CF_3)C{=}C(CF_3)H]$, which is too stable to be decomposed to 1,2-bis(trifluoromethyl)but-2-ene.

Scheme I



Although preliminary data suggest that this method can be used for the preparation of *trans* olefins from acetylenes, further work is in progress to study the scope of the reaction and also to correlate the effect of solvent on the nature of the product.

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The Peracid Oxidation of Acetylenes. 1,2-Methyl Migration, Cyclopropane Formation, and Stereoselective 1,5- and 1,6-Transannular Insertion[1]

Sir:

Although the peracid oxidation of olefins has been thoroughly studied, relatively little is known concerning the chemistry and mechanism of peracid oxidation in the acetylene series.[2] We report here the first examples of 1,2-methyl migration, cyclopropane formation, and stereoselective 1,5- and 1,6-transannular insertion in the peracid oxidation of acetylenes. We have investigated the reaction of di-*t*-butylacetylene (**1**) and cyclodecyne (**3**) with *m*-chloroperbenzoic acid (MCPBA) and compared the results with those obtained

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(1) This work was presented in part at the 158th National Meeting of the American Chemical Society, New York, N. Y., Sept 7-12, 1969, Abstracts, ORGN-152.

(2) (a) V. Franzen, *Chem. Ber.*, **88**, 717 (1955), and previous papers; (b) R. N. McDonald and P. A. Schwab, *J. Amer. Chem. Soc.*, **86**, 4866 (1964); (c) J. K. Stille and D. D. Whitehurst, *ibid.*, **86**, 4871 (1964).