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THE REDUCTION OF INERT FREE RADICALS WITH ASCORBIC ACID.
THE REACTION WITH PERCHLOROTRIPHENYLMETHYL RADICAL

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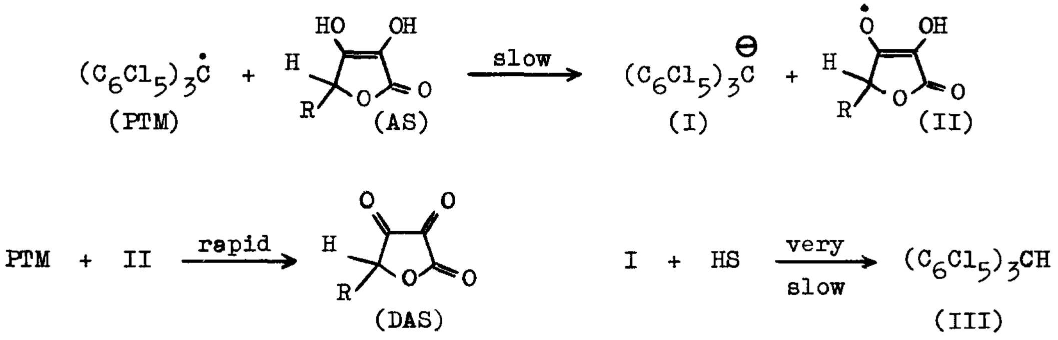
The so-called inert free radicals are trivalent-carbon species which withstand aggressive chemicals such as concentrated sulfuric or nitric acid, halogens, and others.[1] However, they are active in electron-transfer processes: perchlorotriphenylmethyl (PTM) radical can be oxidized to perchlorotriphenylcarbonium ion or reduced to perchlorotriphenylcarbanion; salts of these ions have been isolated in the pure state.[2a,b] Since nitroxide free radicals undergo easy reduction with ascorbic acid,[3] it was considered of interest to test the stability of PTM towards such a biochemical component.

Ascorbic acid (AS) rapidly reduces PTM in aqueous THF at room temperature. It has been found that one mole of PTM requires a minimum of half a mole of the former for complete reduction, and that the product is αH-tetradecachlorotriphenylmethane (III). Yields: 97.6% (1:1 molar); 89.0 (1:0.5); ~50.5 (1:0.25). Perchlorotriphenylcarbanion (I) is detected (visible spectrum[2b]) as a stable intermediate which is slowly (hours) protonated to (III). (I) is stable towards neutral or alkaline water.[2b] On the other hand, AS is converted into dehydroascorbic acid (DAS)[4] which has been isolated.

Since PTM is a one-electron acceptor, these results indicate that the oxidation of AS by PTM takes place stepwise. In this connection it is mentioned that the transient radical (II) has been detected by epr in an oxidation of AS.[5] Under the present reaction conditions, its spectrum cannot be observed on account of its great unstability. Overlap with the strong epr absorption of remaining PTM would probably have prevented its detection anyway.

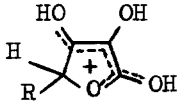
Kinetic measurements on the reaction of PTM (1.68 to 2.68 mmolar) with an excess (8.74 to 19.6 mmolar) of AS in THF:H_2O (10:1 volume) at 20.0 ± 0.5°C have been run following the decay of the former by the epr technique. Up to 50% completion, the kinetic data fit extremely well with an overall second order rate (first order in each reaction component; rel. mean sq. deviation, $\overline{\Delta k/k} < 0.4\cdot 10^{-2}$). Comparison of the rates of each individual run clearly shows this second order correlation (k = 3.09 $\pm$ 0.18 lit mol^{-1} min^{-1}).

The following mechanism is consistent with the experimental results and data:



R = CH(OH)-CH_2OH; HS = protonated species (ascorbic acid, oxonium ions, etc.)

The kinetic results are not consistent with the assumption that ascorbate ion is the reducing species, although in the presence of alkali the reduction of PTM takes place at an extremely high rate. Conversely, in strongly acidic THF (HCl, CF_3CO_2H) the reduction takes place very slowly. This and the uv spectrum data suggest the conversion of AS into its mesomeric protonated form



Other organic reducing species, such as oxalic acid or glucose, do not reduce PTM under the conditions described here. Additional work is presently being performed.

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