The Photo-oxidation of Alkanes by Nitrobenzene

By JONATHAN W. WELLER and GORDON A. HAMILTON*
(*Department of Chemistry, The Pennsylvania State University, University Park, Pennsylvania* 16802)

Summary Alkanes are photo-oxidized by nitrobenzene in good yields to alcohols and carbonyl compounds; the reaction characteristics indicate that the mechanism of the oxidation involves initial hydrogen atom abstraction from the alkane and subsequent reactions of the alkyl radical.

As a result of our continuing interest in the mechanisms of alkane oxidations in organic[1,2] and biological[3–5] systems, we have surveyed a number of possible photochemical oxygen atom transfer reactions, and have observed the ready photo-oxidation of alkanes by nitrobenzene. Although it has recently been reported that various amine *N*-oxides will photo-oxidize alkanes[6,7] the literature gives no indication that nitrobenzene will do the same. There are several reports, however, on the photo-oxidation of olefins[8,9] and diphenylacetylene[10] by nitrobenzene. In an attempt to gain more information on possible mechanisms for oxygen atom transfer reactions, we have studied some of the characteristics of the alkane photo-oxidation by nitrobenzene, and the results are reported here.

All reaction solutions (*ca.* 4 ml), contained in quartz cuvettes (1 cm path length) sealed with rubber septums, were flushed with N_2 for 20 min to remove O_2. The cuvettes were then attached to a 450 w Hanovia high-pressure quartz mercury-vapour lamp at *ca.* 4 cm from the centre of the light and the whole system was immersed in a water bath at 16—18°. The initial nitrobenzene concentration was *ca.* 10 μmoles/ml in the reacting hydrocarbon as solvent, and all analyses were performed by g.l.c.

The photo-oxidation of cyclohexane by nitrobenzene

Filter	Time of irradiation (h)	Nitrobenzene consumed (μmoles/ml)	Cyclohexanol produced (μmoles/ml)	Cyclohexanone produced (μmoles/ml)
Pyrex	10·5	2·0	2·3	0·6
Corex	5·0	5·2	4·2	1·1
Vycor	1·5	3·1	1·9	0·54
	5·0	6·2	4·4	1·9

In the Table are summarized some results on the photo-oxidation of cyclohexane using various filters to limit the maximum energy absorbed by the sample. The total yield of cyclohexanol and cyclohexanone is *ca.* 50% based on the total oxygen content of the nitrobenzene consumed.

Although this yield does not change appreciably when different filters are used, the oxidation occurs more rapidly with filters that transmit higher-energy light. The ketone to alcohol ratio does not change greatly with time of irradiation or with filter. From other experiments not listed in the Table the following conclusions can be drawn: (i) the cyclohexanone is not formed by further oxidation of cyclohexanol (cyclohexanol in cyclopentane, at a concentration comparable to that formed in the usual reaction, is essentially unreacted and yields no cyclohexanone following 5—10 h irradiation with nitrobenzene present); (ii) cyclohexanone slowly disappears (3% using the Pyrex filter to 23% using the Vycor filter after 5 h irradiation) under the reaction conditions but it does not give cyclohexanol as the product; (iii) no bicyclohexyl is formed (if 1% of the consumed nitrobenzene had given rise to this product it could have been detected); (iv) the photochemical production of cyclohexanol and cyclohexanone is not the result of a photosensitized oxidation by trace amounts of O_2 (these oxidation products are not formed in the absence of nitrobenzene after extended irradiation of the cyclohexane solvent either in the absence or in the presence of a photosensitizer such as benzophenone).

The selectivity of the photo-oxidation toward primary, secondary, and tertiary carbon–hydrogen bonds was determined using 2-methylbutane as the hydrocarbon solvent and methods previously described.[2] With the Pyrex filter the relative reactivity per hydrogen atom is primary : secondary : tertiary = 1 : 19 : 300. With the Vycor filter this ratio is 1 : 7 : 110.

The photo-oxidation of either pure *cis*- or *trans*-1,2-dimethylcyclohexane with nitrobenzene leads to the same ratio (1·6) of *cis*- to *trans*-tertiary alcohols. This indicates that the reaction does not proceed with retention or inversion of configuration but rather through some intermediate which allows configurational equilibration.

The above results suggest that the mechanism of the photo-oxidation involves initial hydrogen atom abstraction by photo-excited nitrobenzene, and subsequent reactions of the alkyl radical with nitrobenzene. For these latter reactions several pathways which lead to alcohol and carbonyl products can be envisaged. Attempts to clarify the nature of these steps by isolating the reduction products of nitrobenzene were unsuccessful; apparently a number of reduction products including polymers are formed. Although it has been suggested[7] that the photo-oxidation of alkanes by *N*-oxides proceeds by an oxygen atom insertion process, it is clear from the stereospecificity results reported here that this mechanism does not hold for the photo-oxidation by nitrobenzene.

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