The role of dioxygen in acid-catalysed hydrocarbon conversions

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Molecular oxygen present in acid media is supposed to initiate the catalytic conversion of hydrocarbon substrates via radical cation formation.

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1. Introduction

As early as in 1946, Pines et al. [1] discovered that some reactions of alkanes catalysed by aluminium halides cannot proceed in darkness. In addition, these processes were found to be enhanced by the presence of molecular oxygen. Later, similar results were obtained by Leftin et al. [2] and Kazansky et al. [3] in their studies of the interaction between phenylmethanes and aluminosilicates using a UV spectroscopy technique. The authors of ref. [3] have also established that the addition of oxygen results in a substantial increase in reaction rates for cyclohexane isomerization and toluene disproportionation on acid zeolite catalysts.

All these processes, as being catalyzed by acids, are traditionally believed to occur via carbonium or carbenium ion intermediates. However, the light and oxygen sensitivities of such reactions imply that at least some of the elementary steps are redox in nature. On the other hand, almost all of the acid catalysts that are widely used for hydrocarbon conversions exhibit a more or less pronounced capability to perform a single electron transfer (SET) resulting in the formation of radical ion species [4]. This enables us to suggest that a SET mechanism might play a key role in acid-catalysed hydrocarbon transformations. Such a notion is evidently alternative to the ionic mechanisms commonly accepted for these reactions.

In view of this consideration, it was decided to test the catalytic ring opening using phenylmethylcyclopropane (PMCP) as a substrate and trifluoracetic acid (TFAA) as a catalyst.

2. Experimental

All catalytic experiments were carried out in a glass vacuum system at room temperature. The volume ratio of PMCP to TFAA was 10 : 1, the reaction time was 1 h. Prior to use, the phenylmethylcyclopropane (PMCP) was purified by passing it through a column with freshly calcined SiO_2. Unreacted PMCP as well as the reaction products were collected in a liquid nitrogen trap and, after defreezing, were analysed by using a GLC technique (60 m capillary column coated with Carbowax 20).

ESR measurements were performed on a Jeol JEF-3BF-Q spectrometer. The spectra were recorded at 77 K. UV spectra were recorded using a Cary 17 spectrophotometer.

3. Results and discussion

Cyclopropane hydrocarbons are very suitable model substrates for the study of acid catalysis since their transformation occurs at room temperature and is easy to monitor. As for TFAA, it seems to be strong enough ($pK_a = 0$) to protonate the cyclopropane molecule. On the other hand, this acid exhibits an almost unique ability to bind and activate molecular oxygen, so that it is widely used as a mild oxidizing agent. In addition, TFAA is known to stabilize radical cation species which form under γ-radiation [5,6].

Thus, such a "bifunctionality" of TFAA could facilitate both proton and electron transfer to and from an appropriate substrate. What is more important, these functions are easy to separate from each other by a simple experimental procedure, and thereby the contribution of both acid and redox mechanisms to the transformation of a test molecule could be estimated.

Three series of experiments were performed. In the first set of tests, the reagents were used as such, i.e., without special deoxygenation. In the second set, both TFAA and PMCP were thoroughly freeze–pump–thawed prior to allowing the acid into the ampoule with hydrocarbon. In the last set, the traces of dioxygen were removed from both reagents by adding KI.

The experiments of the first series resulted in a deep red product whose color changes to light yellow after adding water. In the second and third sets, the reaction mixtures were colorless.

When molecular oxygen was present in the reaction system, even as traces, GLC analysis showed the formation of three products, which were identified as dibutyldiphenyl isomers. The conversion of PMCP was 100% with non-purified TFAA and 70% with partially deoxygenated substances.

However, the most amazing result was obtained with a fully deoxygenated reagent. In this case, no trace of reaction products was detected, which implies that strong TFAA cannot catalyse the ring opening unless molecular oxygen is present in the reaction vessel.

ESR spectra of MPCP in TFAA with dissolved oxygen exhibit a poorly resolved signal with $g = 2.0$ and $\Delta H = 19$ G which can be hardly assigned to monomeric or dimeric cyclopropane radical-cation species registered in frozen freon matrices at 77 K under γ-radiation [6]. In the case of the thoroughly deoxygenated reaction mixture, no ESR signals were registered.

A plausible explanation for all these observations could be found if one takes into account the relevant results of Shida et al. [7], who showed that the monomolecular rearrangement of the pale yellow cyclopentane radical cation in freon matrices yields a deep red product with an open structure. This reaction was found to be photoassisted by light at 420 nm. The dark reaction results, however, in the formation of cyclopentane radicals rather than radical cations.

In our case, the oxygen-assisted conversion of PMCP could also be supposed to occur via radical cation intermediates whose formation is strongly enhanced when even traces of dioxygen are present in the reaction system. Otherwise, the TFAA alone does not catalyse this reaction and, at least phenomenologically, demands a co-catalyst to be involved. This provides evidence that the SET mechanism could be operative when the initial step of an acid-catalysed reaction is considered.

This suggestion is strongly supported by some other results we obtained with color indicators. Triphenylmethane and triphenylcarbinol, when in contact with deoxygenated TFAA, did not show any change in color which would be characteristic of pure acid–base interactions. In contrast, both indicators become bright yellow if contacted with the acid containing dissolved oxygen.

In conclusion, all these findings seem to have a simple mechanistic explanation if one accepts the notion that the radical-cation formation might be an initial stage of acid-catalysed hydrocarbon conversion.

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