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Joint Homogeneous and Heterogeneous Catalysis: a New Synergistic Effect

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Summary An increase of the order of 10^4 in the rate of the Menschutkin reaction was achieved at reaction sites created by the adsorption of silver ions on silver iodide or carbon surfaces.

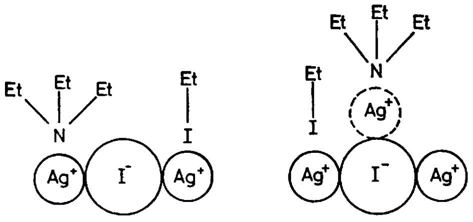
HOMOGENEOUS and heterogeneous catalyses are generally regarded as quite separate phenomena. We report below a co-operative effect between the two types which can be more powerful than either type alone. In the case described, suitable sites for a reaction were created by the adsorption of the homogeneous catalyst on the appropriate surface positions of the solid catalyst. The knowledge that such a synergistic effect exists should allow synthetic chemists to invent similar tailor-made catalytic conditions for other reactions.

This research concerns the Menschutkin reaction (1).

$$Et_3N + EtI \rightarrow Et_4N^+I^- \qquad (1)$$

Reactions like these, used for the synthesis of tetra-alkylammonium salts, proceed only slowly at ordinary temperatures.[1] A search was therefore made for possible heterogeneous catalysts for reaction (1). Kinetic experiments were carried out at *ca.* 20 °C with 0·10 M (M≡mol dm^{-3}) Et_3N and 0·10 M EtI in 10 cm^3 AnalaR benzene solution, the reaction being followed by Volhard titrations for iodide using 0·020 M $AgNO_3$ and 0·020 M KSCN solution. The results were disappointing: SiO_2 (B.D.H., washed with perchloric acid, 0·2 g) and Al_2O_3 (Spence type H, well washed and dried, activated at 450 °C, 100—500 μm, 0·2 g) had little or no effect on the rate whereas the reaction was actually inhibited by carbon (Black Pearls 2, 76—152 μm, 0·3 g), HgS (BDH, $<$ 152 μm, 1 g), and AgI (prepared as in ref. 2, 1 g). The silver iodide caused a 50% fall in the rate. These findings suggested non-reactive adsorption of the reactants, an explanation supported by independent adsorption experiments.

A search for a suitable homogeneous catalyst in benzene was more successful. At 25 °C, a 25 cm^3 benzene reaction mixture 0·020 M in EtI and 0·029 M in Et_3N formed only 3% of product (in terms of EtI) in 46 h. When the benzene solution was also made 0·020 M in $AgNO_3$, 17% of reaction took place in 1·5 min. The reaction was speeded up even further when the soluble silver salt and a suitable solid were both present. Thus, in 1·5 min, the addition of 0·020 M $AgNO_3$ and 0·18 g of AgI produced 35% of product; 0·020 M $AgNO_3$ and 0·18 g of carbon 70% of product. This synergistic effect is the more pronounced when it is remembered that addition of silver nitrate by itself automatically formed insoluble AgI as the reaction progressed. The only water-soluble product of the catalysed reaction proved to be Et_4NNO_3.



(A) (B)

FIGURE

These results can all be explained by a simple mechanism. Consider the situation with a polar solid like AgI (Figure, A). The Et_3N and EtI molecules should adsorb on the surface by their functional groups which are both bases (in the Pearson SHAB sense[3]). The molecules will therefore sit on next-nearest Ag^+ acid sites too far apart to allow chemical interaction. Even if they were adsorbed on neighbouring positions (as on a carbon or a metal with large ions), their relative orientations would be unfavourable for the iodide ethyl group to bond to the amine nitrogen. This picture makes plain why the addition of solids by themselves caused adsorption of reactants but no catalysis. A more favourable orientation for reaction could, however, be attained if the adsorbed amine were raised one atomic layer higher. This is likely to have been the effect of introducing the soluble silver salt; silver ions would then adsorb on iodide sites of the AgI surface and amine molecules could adsorb on top of these adsorbed Ag^+ ions (Figure, B). The EtI and Et_3N molecules now sit next to each other, suitably positioned for reaction.

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