

washed in benzene. The amount of reaction or adsorption which had taken place after each extension was determined by measuring the radioactivity on the surface of the specimen. This measurement was made in the centre of the specimen using an end-windowed Geiger-Müller counter of 0.2 in. diameter. Only the results obtained with stearic acid will be discussed here.

Fig. 1 shows the effect of deformation on the rate of adsorption of stearic acid on copper. The increased rate of adsorption on the deformed surface can be seen. Fig. 2 shows the effect of deformation on the rate of adsorption of stearic acid on iron. The increased rate of adsorption on the deformed surface is again evident. All three metals showed enhanced reactivity resulting from deformation and there was an approximately linear relation between the increase in adsorption on the deformed surfaces and the amount of deformation. In the experiments with aluminium the increase in reactivity was most marked if the deformation was carried out at the smaller rate of strain, due perhaps to the development of coarser slip in the metal under these conditions.

The increase in reactivity was not observed in specimens which were extended and then annealed before being allowed to interact with the solutions; the effect is thus not simply one of increased surface area resulting from deformation. Nor was increased reactivity observed in specimens which had been quenched from 600° C into cold water before allowing them to interact with the solutions. Such specimens would contain a large number of point defects; the effect is, therefore, not due to the creation of point defects in the deformed metals.

The effect is similar to that reported by Uhara *et al.*¹, who showed that the ability of copper wire to catalyse the decomposition of diazonium salts was enhanced by torsional deformation. They attributed this to a higher dislocation content of the deformed metal. It seems probable that the increased reactivity found in the present experiments is also due to a higher dislocation content.

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¹ Uhara, I., *et al.*, *Nature*, **192**, 867 (1961).

CRYSTALLOGRAPHY

Charge-Transfer Complex Crystal Growth at a Solution-Solid Interface

ORIENTED intergrowth (epitaxy) of organic compounds has been reported in many hundreds of cases¹. Although some examples seem to involve van der Waals forces exerting an orienting effect², a more generalized description might be that on a solid surface anisotropic short-range forces can exist which will cause orientation of molecules on this surface.

In an attempt to deposit from solution oriented crystals of an electron donor, 1,4-diaminodurene, on an electron acceptor single crystal, *p*-chloranil, it was found that crystals of the 1 : 1 charge-transfer complex^{3,4} were deposited instead. For example, when 6.8×10^{-5} M diaminodurene in petroleum ether is placed in contact with a chloranil crystal at 25°, small crystals of the complex are observed to grow first on the surface of the crystal and then on one another. Exhaustion of the amine is substantially complete in one day. Concentrations of amine 5–10 times higher lead to a deposit of amorphous complex; solutions 10 times as dilute gave some colour in solution but no deposit on the crystal.

Similar crystal growth occurs when compacted disks (0.5 g compacted at 3,000 atm. in a 13 mm die) of the amine and the quinone are placed a few mm apart in a poor solvent such as petroleum ether, the residual chloranil tablet becoming covered with a dense network of weakly held, randomly oriented needles of the complex in a few days. A beard-like stubble of crystals appeared on the edge of the chloranil tablet within minutes of submerging the pellets. Nucleation continued, first on the remaining chloranil surface and then by crystals growing on one another.

These observations all suggest that crystal growth is occurring in a small concentrated zone near the least soluble component in solution, but that there is some tendency for orientation to occur on the surface of that component.

In principle, this constitutes a novel technique of growing crystals in a controlled manner. In light of the difficulty of obtaining even small crystals of charge-transfer complexes which are regular enough for structural and electrical investigations⁴, this technique of crystal growth is being further investigated. Thus far it appears that the early stages of growth seem to be quite regular but the crystal ends have a distinct tendency to grow two or more parallel spikes, that is, one crystallographic direction is favoured for growth.

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¹ See Seifert, H., in Gomer, R., and Smith, C. S., *Structure and Properties of Solid Surfaces* (Univ. of Chicago Press, Illinois, 1953).

² Willems, J., *Z. Elektrochem.*, **56**, 345 (1952); *Z. Kristallog.*, **105**, 53, 144, 149, 155 (1943).

³ Labes, M. M., and Ur, H., *J. Org. Chem.*, **26**, 4760 (1961).

⁴ Kronick, P. L., and Labes, M. M., *J. Chem. Phys.*, **35**, 2016 (1961).

CHEMISTRY

Heterogeneous Recombination of Free Atoms

RECENT work by Reeves *et al.*¹ has shown that, under certain conditions, electronically excited molecules of O₂, N₂, NO, etc., can be formed by the heterogeneous recombination of free atoms on a metal surface. In these experiments light emission was observed from the gas just above the metal surface, showing that the molecules formed were desorbed in an excited electronic state. This evidence, and data on the kinetics of heterogeneous recombination^{2,3}, suggest that this desorption process is very rapid and that the molecules liberated may have excess kinetic energy. In this communication we report on an unsuccessful attempt to obtain evidence for such excess kinetic energy, by comparing the pressure exerted by a mixture of atoms and molecules on a surface where recombination takes place with the pressure on a surface where recombination is negligible.

The apparatus used consisted of metal foil 3 cm long, 1 cm wide and 0.1 mm thick mounted on a thin vertical glass or quartz fibre. Half of each face of the vane was coated with clear glyptal resin, which has a low coefficient for recombination of atoms, the coating being applied so that any differences in apparent pressure on the two types of surface would result in a couple on the vane. Deflections of the vane were observed by means of a small galvanometer mirror mounted on the centre of the vane. The products of an electrodeless radiofrequency discharge through oxygen, nitrogen or hydrogen flowed vertically past the vane. Total pressures between 0.5 and 2 mm mercury were used, and atom concentrations of up to 20 per cent corresponding to atom flows of up to 8 μmole/sec were obtained.

The atom concentrations were determined by gas phase titration^{4,5}, and the fraction of atoms recombining on the