b) At high surface coverage ($\Theta = 0.1$ to 1.5), determination of surface diffusion coefficients D_s from measurements of the adsorption velocity in a large number of pores (Aerosil disk) by means of a vacuum sorption balance. Examples: Ar, N_2, and organic molecules. For benzene and cyclohexane between 15 and 55 °C the D_s values are of the same order as the diffusion coefficients in liquids (10^{-5} cm²/sec). At all temperatures there is a distinct maximum at about half a monomolecular layer. Examples, at 52 °C: benzene at $\Theta = 0.4$, $D_s = 2.0 \times 10^{-5}$ cm²/sec; cyclohexane at $\Theta = 0.3$, $D_s = 2.1 \times 10^{-5}$ cm²/sec. This is explained by the fact that the activation energy for surface diffusion at first diminishes rapidly (from 70 % of the adsorption energy at $\Theta \approx 0.1$ to about 40 % at Θ 0.5) and that D_s increases correspondingly (filling of energy holes). As the coverage increases further the probability of place exchange of the adsorbed molecules decreases and D_s becomes correspondingly lower.

c) Determination of relaxation times from measurements with a nuclear resonance impulse spectrometer on the same samples as were used for measurement of D_s. The spin-spin relaxation times for benzene in the temperature range studied lies between that of the liquid (T_2 about 50 sec) and of the solid state (T_2 about 10 µs); for benzene adsorbed on Aerosil ($\Theta = 0.68$) at -60 °C, $T_2 = 10$ ms; at $+100$ °C, $T_2 = 80$ ms.

Lecture at Hamburg (Germany) on May 25th, 1967   [VB 90 IE]
German version: Angew. Chem. 79, 908 (1967)

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Structure, Preparation, and Properties of Cyclopolyphosphines

By L. Maier [*]

Although many cyclopolyphosphines containing aliphatic substituents have been prepared during recent years, among those with aromatic substituents only the phenyl derivative has been closely characterized [1]. Phenylcyclopolyphosphine, $(C_6H_5P)_x$, occurs in various forms, with melting points (A) 150 °C, (B) 190 °C, (C) 252–256 °C, and (D) 262–285 °C. It has been shown by X-ray structure analysis that form A is pentaphenylcyclopentaphosphine, in which the phosphorus atoms form an equilateral pentagon with approximate m symmetry. Form B occurs in at least four crystal modifications, all having the structure of hexaphenylcyclohexaphosphine with the phosphorus atoms forming a six-membered ring in the chair conformation. Forms C and D give the same Debye diagram and are highly crystalline [2], but their structures are not known.

Depending on the reaction conditions, treatment of $ClC_6H_4PCl_2$ with $ClC_6H_4PH_2$ gives three (chlorophenyl)-cyclopolyphosphines of formula $(ClC_6H_4P)_x$ with melting points (A, from ether) 191–193 °C, (B, from benzene) 194–198 °C, and (C, no solvent) 161–165 °C. Determination of the molecular weights in exaltone (cryoscopic) and benzene (osmometric) shows that the phosphorus rings are five-membered in form (A), six-membered in form (B), and four-membered in form (C).

So far, two forms of the o-tolyl compounds $(o\text{-}CH_3C_6H_4P)_x$ have been isolated, the melting points being (A) 290–299 °C and (C) 198–202 °C. Determination of the molecular weight in $CHBr_3$ indicates a five-membered phosphorus ring for form (A). Form (C) crystallizes in the tetragonal system, probably of space group $J\overline{4}$ with parameters $a = b = 12.89$, $c = 7.60$ Å; there are eight $o\text{-}CH_3C_6H_4P$ units in the unit cell. Although the possibility that C is monomeric or dimeric

cannot yet be excluded, it is very probable that this form contains a four-membered phosphorus ring.

Lecture at Würzburg on July 7th, 1967   [VB 93 IE]
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Experiments on the Scattering of Molecular Beams for the Study of Reactions of Potassium with Methyl Iodide, Hydrogen Bromide, and Bromine

By J. P. Toennies [*]

Theoretical and experimental developments have led to marked advances in the study of gas-phase reactions during the last few years. Particular interest attaches to work on the determination of reactive collision cross-sections (σ) by means of scattering experiments with crossed molecular beams. Reactive collision cross-sections are important for the theory of chemical reactions because they are dependent on the interaction potential $V(R)$ between all the atoms taking part in the reaction and are thus the only quantities that afford direct information about this potential. The relation between the potential and the cross-section is derived by classical calculations of trajectories. The cross-sections obtained from experiments on the scattering of molecular beams have made it possible, for the first time, to study the connection between the interaction potential and the reaction constants.

For experimental reasons, the scattering of molecular beams can at the present time only be used for study of those reactions involving at least one alkali atom (M). The exothermic reaction

$$K + CH_3I \rightarrow KI + CH_3 \quad (\Delta E = -22 \text{ kcal/mole})$$
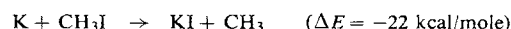
has been studied by the molecular beam method and has also been very recently subjected to intensive theoretical investigation by trajectory methods.

The angular distribution of the KI formed indicates that the reaction occurs mainly during the central collision in which the K atom is reflected backwards with capture of the I atom. The collision process can thus be described by the following diagram:

K	$\rightarrow$ $\leftarrow$	ICH_3	Before
KI	$\leftarrow$ $\rightarrow$	CH_3	After
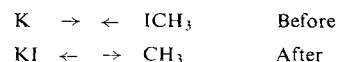
The backward scattering observed indicates a short reaction time ($\tau < 10^{-12}$ sec), so that the reaction does not proceed by way of an activated complex as postulated by the Eyring theory. The velocity of the KI shows that most of the reaction energy is used for internal activation of the KI molecule. Similar results have been obtained for the reaction between K and HBr.

Bunker and Karplus and co-workers have carried out extensive trajectory calculations for the $K + CH_3I$ reaction. They calculated reactive cross-sections for five potential models, of which one was shown to be satisfactory by comparing the experimental cross-section with the corresponding theoretical values; with this model the whole of the reaction energy becomes free when the distance between K and the I of CH_3I amounts to about 4 Å. In this way the first determination of the interaction potential for a reaction was made.

The potential model agrees well with the view that one electron

$$K + ICH_3 \rightarrow K^{\oplus} + I^{\ominus}CH_3 \rightarrow KI + CH_3$$
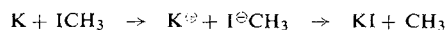
jumps from the potassium atom to the CH_3I. The strong attraction between the resulting ions explains why the reaction energy is liberated before the products are formed.

The electron-jump mechanism, which is also known for reactions in the liquid phase, was first used by *M. Polanyi* as early as the 1930's to explain the high velocities of reactions of the type $M + X_2$ observed in sodium flames. The results of molecular beam studies of this type of reaction agree well with the cross-section found by *Polanyi*. Molecular beam measurements also show that the products of this reaction

are scattered forwards, as is to be expected from the large cross-section.
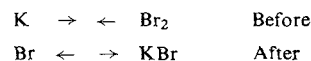
| K | $\rightarrow$ | $\leftarrow$ | Br_2 | Before |
| Br | $\leftarrow$ | $\rightarrow$ | KBr | After |

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SELECTED ABSTRACTS

The formation of 2-oxazolones by photorearrangement of 3-hydroxyisoxazoles has been observed by *H. Göth, A. R. Gagneux, C. H. Eugster*, and *H. Schmid*. UV irradiation of aqueous solutions of ibotenic acid *(1)* from toadstools leads in 35% yield to muscazone *(2)*, an α-amino acid that has been
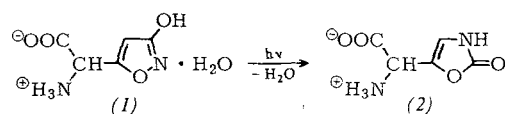
isolated from *Amanita muscaria*. Similarly, UV irradiation of muscimol (5-aminomethyl-3-hydroxyisoxazolone), another active principle from *Amanita* leads to 5-aminomethyl-2-oxazolone (15%), together with 3-hydroxy-5-hydroxymethylisoxazole. 3-Hydroxyisoxazoles, *e.g.* 3-hydroxy-5-methylisoxazole, can be obtained from ethyl 3,3-bis(methoxy)butyrate by conversion into the hydroxamic acid and ring closure by heating under vacuum or with HCl gas in anhydrous methanol or glacial acetic acid. / Helv. chim. Acta *50*, 137 (1967) / —Ma.   [Rd 653 IE]

A 1,4-photoaddition of pyrrole to benzene was observed by *M. Bellas, D. Bryce-Smith*, and *A. Gilbert*. UV irradiation of solutions of pyrrole in benzene at 25 °C under nitrogen led to a mixture of 1:1 adducts, about 95% of which consisted of a colorless compound having the constitution *(1)*, m.p. 15 °C. The compound is practically non-basic, and is not attacked by dilute mineral acids. On catalytic hydrogenation it gives 2-cyclohexylpyrrole and a trace of 2-phenylpyrrole. *(1)* is
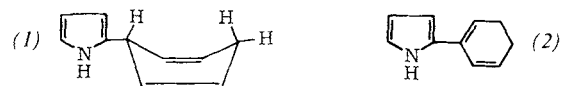
rearranged by potassium t-butoxide into an unstable diene, probably *(2)*. The assumed constitution *(1)* is in agreement with the UV and NMR spectra. / Chem. Commun. *1967*, 263 / —Ma.   [Rd 685 IE]

The Protein Sequenator described by *P. Edman* and *G. Begg* is an instrument for automatic amino-acid sequence analysis. It was used to automate the "Edman degradation", *i.e.* the reaction of the N-terminal amino acid of a peptide chain with phenyl isothiocyanate and conversion of the adduct into the peptide chain having one amino acid less and the 2-anilino-thiazolin-5-one derivative of the amino acid removed. This is delivered to a fraction collector, converted outside the Sequenator into the 3-phenyl-2-thiohydantoin, and identified by thin-layer chromatography. One reaction cycle, *i.e.* the

removal of one amino-acid residue from a peptide chain, involves 30 operations and takes 93.6 min. The average yield per cycle has so far been 98.5%; this permits about 100 cycles, and hence the sequence analysis of a protein consisting of 100 amino acid units. The reaction vessel, which is maintained at 50 °C thermostatically, consists of a glass beaker rotating at a constant speed of 1425 r.p.m., in which the reaction solution covers the wall in the form of a film. With this arrangement, the necessary technical operations such as dissolution, evaporation, vacuum drying, and extraction can be carried out in such a way that the protein always remains in the reaction vessel.

The Sequenator was used for the sequence analysis of humpback-whale apomyoglobin. 5.0 mg of protein were sufficient. The analysis was allowed to proceed for 60 cycles, and it was found that within this sequence of 60 amino acids, six were interchanged in relation to the sequence in sperm-whale myoglobin. / Europ. J. Biochem. *1*, 80 (1967) / —Hö.

[Rd 683 IE]

A Meisenheimer complex *(2)* containing only one nitro group has been detected by *R. Foster, C. A. Fyfe, P. H. Emslie*, and *M. I. Foreman* by NMR spectroscopy. The addition of sodium methoxide to 9-nitroanthracene *(1)* in dimethyl sulfoxide yields a deep red solution ($\lambda_{max} = 505$ nm), and a band appears in the NMR spectrum at -4.96 ppm, whereas the absorption of the hydrogen in position 10 of *(1)* is situated at -8.92 ppm.
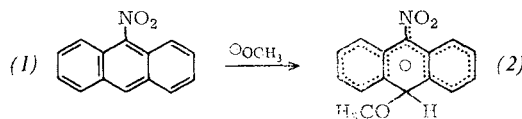
The absorption of the protons in positions 1 and 8 is shifted from -8.2 ppm to -8.8 ppm, and the multiplet due to the remaining hydrogens is shifted from -7.75 to -7.16 ppm. Meisenheimer compounds from dinitrophenyl ether and methoxide and from trinitroaromatic compounds and acetonate (color carriers of the Janovski reaction) exhibit similar NMR-spectroscopic behavior. / Tetrahedron *23*, 227 (1967) / —Bu.   [Rd 667 IE]

Diazoacetaldehyde *(1)* was synthesized by *Z. Arnold* by heating β-N-methylanilinoacrolein *(2)* with excess p-toluenesulfonyl azide at 70—80 °C under vacuum, whereupon diazoacetaldehyde *(1)* distilled off [pure *(1)* detonates violently when overheated!] (yield approx. 70 %). *(1)* can be purified by vacuum distillation (bath temp. < 50 °C) or by extraction from aqueous solution with methylene chloride; it is a yellow liquid having b.p. 40 °C/10 mm, and is stable at

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