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THE ORIGIN OF SOME IRREPRODUCIBILITIES IN THE KINETIC STUDY OF THE REACTION $W(CO)_5$ (ANILINE) + $P(C_6H_5)_3$

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Summary

The title reaction has been examined under strict exclusion of light and air, but the rate was still found to be irreproducible. The variability can be ascribed in part to the unavoidable presence of traces of triphenylphosphine oxide in triphenylphosphine.

The thermodynamics of the reaction $W(CO)_5$ (aniline) + $P(C_6H_5)_3 \rightleftharpoons W(CO)_5$-$P(C_6H_5)_3$ + aniline in toluene have been examined by Angelici and Ingemanson [1]. Two aspects of this work deserve some closer examination: (1) the results are poorly reproducible, and (2) the equilibrium entropies are very high (up to 90 e.u.) which is a surprising result for a reaction where ΔS would be expected to be nearly zero, since there is no change in the number of molecules and the species involved have similar polarities. Moreover, a ΔS of 90 e.u. implies that the $\Delta S^{\ddagger}$ of the forward and backward reaction should differ by that amount (whatever the mechanism), which is highly improbable.

We have reexamined this reaction and found that $W(CO)_5[P(C_6H_5)_3]$ does not react with aniline under the conditions in which equilibrium is said to be attained in two days. Typically, a toluene solution of phosphine complex (1.96×10^{-3} *M*) and aniline (1.45×10^{-1} *M*) should lead, according to the value of the equilibrium constant, to a 1.45×10^{-3} *M* concentration of the aniline complex; since this latter shows an extinction coefficient of 3300 at 410 nm, it should thus exhibit an absorbance of at least 3.0. After three days in complete darkness at 45.7°C, the measured absorbance was less than 0.1, and the absorption spectrum was still that of the original solution. This experiment has been repeated several times and is thus firmly established.

When the cell was removed from the spectrophotometer and exposed to laboratory light, a yellow colour rapidly developed; when we attempted to measure the rate of this process, the reaction was found to stop abruptly when the cell was placed back in the spectrophotometer but successive exposures to light increased the absorbance of the yellow substance. The absorption spectrum of the resulting solution was different from that of pure $W(CO)_5$ (aniline).

It is thus obvious that the reported equilibrium constants are not true thermodynamic values, but reflect the result of photochemical processes. It is known [2] that the photolysis of $M(CO)_5[P(C_6H_5)_3]$ complexes in the presence of ligands L yields some disubstitution products $M(CO)_4[P(C_6H_5)_3]$ L besides the ligand-ligand exchange product $M(CO)_5L$.

Photochemical reactions such as $W(CO)_4LL' + L'' \underset{h\nu}{\overset{h\nu}{\rightleftharpoons}} W(CO)_4LL'' + L'$ reach a photostationary state, and such pseudo-equilibria are known to depend strongly on the spectral distribution of the incident light; this may of course vary widely according to hour, season or cloudiness, and is definitely different for daylight and artificial light. Since the quantum yield for both the L—CO exchange and L—L′ exchange may depend on the irradiating wavelength [2], but not necessarily in the same way, a solution of phosphine complex + aniline will give, under the action of uncontrolled light, mixtures of varying concentrations of at least four components: the two monosubstituted complexes and the photostationary mixture of the *cis* and *trans* isomers of the disubstituted compound. The inertness of $W(CO)_5[P(C_6H_5)_3]$ towards aniline has independently been noted by Dobson [3].

During these exploratory experiments, it was also found that atmospheric constituents have an influence on the kinetics of the substitution. A plot of log $A_{410\text{nm}}$ vs time was a straight line up to some 70% reaction; it then deviated rather strongly because A_∞ was far from zero, whereas the calculated value for the absorbance of the phosphine complex at 410 nm should be negligible.

We observed that this high A_∞ value was not due to the absorption by a coloured substance, but to a rather strong cloudiness in the cell. When the cells were first thoroughly degassed by successive freeze (77 K)-pump-thaw cycles (residual pressure less than 10^{-3} Torr) and tightly closed, the final A readings were nearly zero and time-independent; this resulted in first-order plots up to 98% reaction. Nitrogen bubbling instead of vacuum degassing still gave appreciable cloudiness.

The spontaneous decomposition of the aniline complex is not greatly affected by atmospheric contaminants. The log A vs. time plot is straight during the first few percent reaction, and then levels off. Here again, degassing avoids the formation of the white suspension. It appears, however, that the rate of this decomposition is much lower than that of the dissociative component of the substitution reaction. The rate constant for this dissociative path was found to be near 2×10^{-4} sec^{-1} at 45.7°C (as compared with 1.98×10^{-4} at 44.8°C [3]), i.e. a half life of approximately one hour; in the decomposition reaction, the absorbance dropped from 0.95 to 0.37 in 23 h. It seems thus that the decomposition reaction of the aniline complex is not correlated with the dissociative mechanism of the substitution, whereas it is found to be so for the corresponding processes in analogous Mo—pyridine and Mo—piperidine complexes [4].

Despite all these precautions, i.e. performing all kinetics in degassed cells and in the dark, the reaction rates remained erratic. A survey of work done in vari-

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* We thank Professors Dobson and Darensbourg for private communications in relation with this problem.

TABLE 1

INFLUENCE OF ADDED TRIPHENYLPHOSPHINE OXIDE ON THE OBSERVED FIRST-ORDER RATE CONSTANT k_{obs} FOR THE REACTION:
$W(CO)_5(aniline) + P(C_6H_5)_3 \rightarrow W(CO)_5[P(C_6H_5)_3]$ + aniline, in toluene at 48°C

$[P(C_6H_5)_3]$[a], (M)	0.35	0.27	0.20	0.08
k_{obs} $(sec^{-1}) \times 10^4$	7.54	6.53	5.45	3.31
Slope: 1.57×10^{-3} l mol^{-1} sec^{-1}		Intercept: 2.13×10^{-4} sec^{-1}		
$[P(C_6H_5)_3]$[b], M	0.40	0.30	0.20	0.10
$[OP(C_6H_5)_3]$, $M \times 10^4$	9.97	9.97	9.97	9.97
k_{obs} $(sec^{-1}) \times 10^4$	12.3	10.8	9.69	7.88
Slope: 1.46×10^{-3} l mol^{-1} sec^{-1}		Intercept: 6.52×10^{-4} sec^{-1}		

[a] Recrystallised four times; initial concentration of complex: 8.4×10^{-4} M.
[b] Recrystallised four times; initial concentration of complex: 8.6×10^{-4} M. Slope and intercept values calculated by the least square method.

ous laboratories shows that irreproducibilities are plaguing authors seeking quantitative [5,6] kinetic results and even qualitative data*, and the origin of these fluctuations is still a problem. A systematic examination of the triphenylphosphine gave some interesting results.

"Pure" triphenylphosphine was always used after two recrystallisations, but thin-layer chromatography showed a faint spot which was identified as due to triphenylphosphine oxide. Three more crystallisations afforded oxide-free phosphine, which led to the lowest rates ever found in our laboratory. Purposely added triphenylphosphine oxide induced a very strong acceleration (see Table 1), but interestingly, the slope of the k vs. [ligand] line is practically independent of the oxide concentration, and only the intercept is affected. If we analyse the rate equation according to the conventional scheme, one would say that $(C_6H_5)_3PO$ accelerates the dissociative component of the phosphine-aniline exchange**. If we assume that the intercept of the "purest phosphine" line represents the true dissociative constant and that the acceleration is first order in Ph_3-PO, one finds a rate constant for the oxide-catalysed reaction near 0.4 l mol^{-1} sec^{-1}, which is a very high value for associative processes; these usually have rate constants in the vicinity of 10^{-3}-10^{-4} l mol^{-1} sec^{-1}.

Systematic experiments have shown however that the "purest triphenylphosphine" oxidises rapidly in toluene solution, and crystals grown under an N_2 atmosphere start showing an oxide spot after a few days, even when kept in the dark. We therefore feel that accurate rate constants for the present substitution reaction will be very difficult to obtain unless one works with the highest precautions to avoid the contamination of the triphenylphosphine. Trace impurities in the solvent may also lead to erratic results, as we have found that the same batch of phosphine dissolved in "pure" toluene of two origins consistently gave rates differing by 15% for the dissociative constant, but less than 1% for k_A. The nature of the oxide-accelerated reaction is presently under study.

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* Venanzi describes the synthesis of $[IrHX(PPh_3)QP]X$ [7a] and has been unable to repeat it [7b]. We thank Prof. L.M. Venanzi for drawing our attention to these results and for friendly discussions.

** It is interesting to notice that trimethylphosphate has been found to accelerate the substitution of Ar in $ArM(CO)_3$ by trimethylphosphite [8].

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