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# THE SOLUTION PHASE DECOMPOSITION OF HEXAMETHYL (DEWAR BENZENE) PALLADIUM(II) CHLORIDE; A PRELIMINARY KINETIC STUDY.

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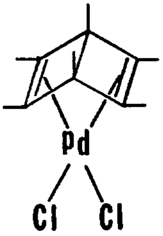
Hexamethyl(Dewar benzene)palladium(II) chloride (1), first reported by Dietl and Maitlis in 1967, was found by those workers to be stable for ca 20 min. at 33° in deuteriochloroform after which time it decomposed rapidly and quantitatively to hexamethylbenzene (2) and palladous chloride.[1] Hexamethyl(Dewar benzene) (3), the uncomplexed ligand, is much more stable than 1 toward isomerization to 2 ($t_{1/2}$ = 105 hr at 120°)[2] possibly because concerted $[\pi^2S + \sigma^2S]$ cycloadditions are symmetry forbidden in the ground state. Hence, Pd(II), under homogeneous neutral conditions, is an efficient catalyst for the aromatization of 3.[3a,b]



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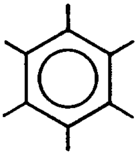

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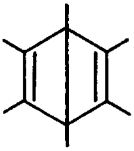

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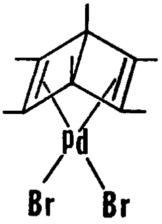

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Catalysis of symmetry restricted reactions by transition metal salts and complexes is well documented. The activity of such species as Ag(I), Rh(I), and Pd(II) was initially attributed to a change in symmetry requirements for concerted transpositions of substrate-metal complexes,[4a-c] but it is now known that most such reactions proceed by multistep pathways.[5a-d,6] The decomposition of 1 has been described as no exception. A kinetic study of that decomposition has not appeared, but Dietl and Maitlis gave some evidence for autocatalysis and proposed an unusual two-step mechanism.[1] Orbital Symmetry control would demand first order kinetics.

We detail herein the first kinetic study of the solution phase decomposition of 1 and report that *the form of the rate law (e.g. first order vs. autocatalytic) and observed rate constants depend on sample history*. The acquisition of reliable kinetic data was complicated by the instability of 1 even when it was handled below room temperature, under nitrogen and in the solid state; in addition to palladous chloride and 2, hydrogen chloride and Pd° were identified as decomposition products Also, separate batches of 1, synthesized by the same procedure, often appeared to differ in purity. The disappearance of 1 was monitored by nmr spectroscopy (Varian A-60 spectrometer), the probe temperature being measured with a standard methanol sample. Our major findings are summarized below.

1) When 1 was prepared under ambient conditions, its disappearance in chloroform (or $CH_2Cl_2$) was autocatalytic thus corroborating the original observations of Dietl and Maitlis.[1]

2) When 1 was prepared from rigorously purified 3 under dry nitrogen and at low temperatures, its disappearance in dichloromethane conformed *moderately well* to a first order rate equation, and there was no induction period as observed with autocatalytic decompositions.

3) Kinetic samples taken from different synthetic batches of 1 which had been stored for several weeks at -78° gave rate constants in reasonable agreement at 21.5° and at 31.5°.

4) One batch of 1 was stored at -10° subsequent to its storage at -78°, and samples were taken for kinetic runs at 21.5° and at 26.5°. The first order rate constants were markedly enhanced.

The rate data (least squares analyses) are summarized in Table 1 while Figures 1 and 2 show a typical first order plot and an autocatalytic decay curve.

The autocatalytic destruction of 1 cannot, by definition, be a concerted reaction, but the first order decomposition of 1 may be concerted and may be a bonafide example of Pd(II) catalysis by the orbital symmetry mode of action. However, a stepwise process which proceeds by rate determining formation of the dipolar intermediate 5 followed by rapid expulsion of palladous chloride from that intermediate (see below) is also plausible and is consistent with the report that the palladium (II) bromide complex 4 is significantly more stable than 1.[7]

Figure 1. First Order Decomposition of (1) at 21.5° (sample 1)

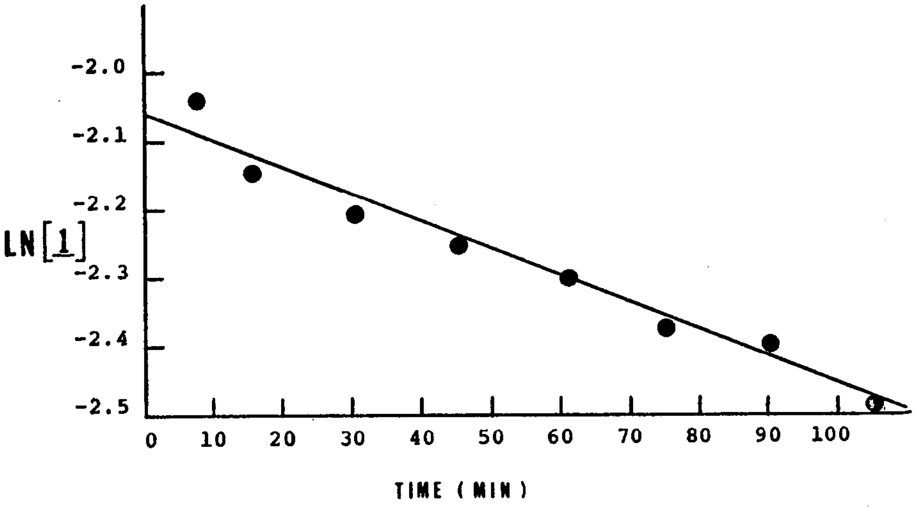
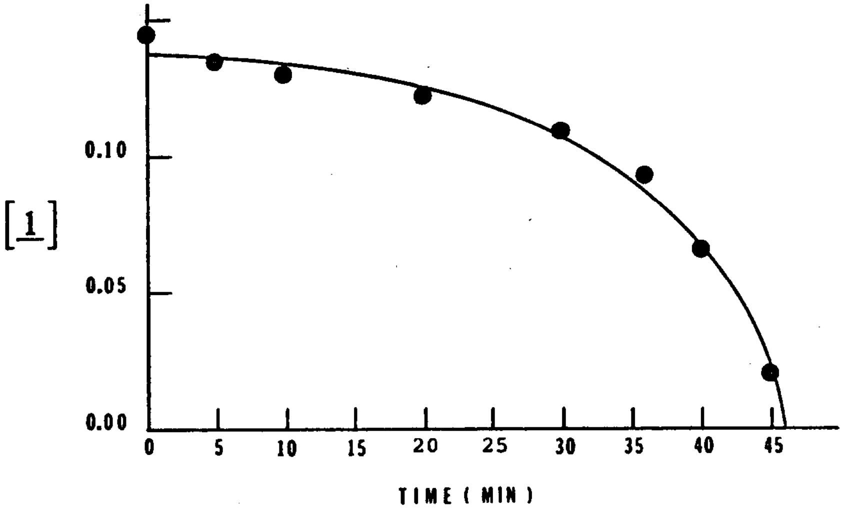


Figure 2. Autocatalytic Decomposition of (1) at ~15°; Molar Concentration vs. Time. (sample 9)



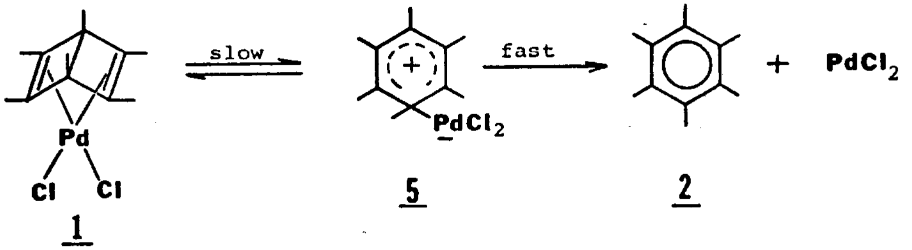


TABLE I

| Sample No. | Batch | Atmos. | Temp. | Days | Reaction Temp. | k (sec$^{-1}$)* | ~% Conversion |
|---|---|---|---|---|---|---|---|
| | **Batch Storage History** | | | | | | |
| 1 | A | $N_2$ | -78° | 38 | 21.5° | 7.0 X $10^{-5}$ | 40 |
| 2 | B | $N_2$ | -78° | 20 | 21.5° | 5.8 X $10^{-5}$ | 39 |
| 3 | C | $N_2$ | -78° | 20 | 21.5° | 5.5 X $10^{-5}$ | 45 |
| 4 | A | $N_2$ | -78° | 25 | 31.5° | 2.7 X $10^{-4}$ | 75 |
| 5 | B | $N_2$ | -78° | 25 | 31.5° | 4.3 X $10^{-4}$ | 85 |
| 6 | C | $N_2$ | -78° | 32 | | | |
| | | | -10° | 42 | 21.5° | 1.9 X $10^{-4}$ | 55 |
| 7 | C | $N_2$ | -78° | 32 | | | |
| | | | -10° | 38 | 26.5° | 2.1 X $10^{-4}$ | 72 |
| 8 | D | Air | -10° | 11 | ~15° | | 70 |
| 9 | D | Air | -10° | 11 | ~15° | | 86 |

*The correlation coefficients were 0.975, 0.937, 0.820, 0.964, 0.961, 0.931, and 0.984 for the first order runs.

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