lizations from ether by cooling in Dry Ice. There was obtained 0.86 g (41%) of yellow prisms, mp 104–105° dec, $\gamma_{CO}$, 1920, 1985, 2055 (vw) cm$^{-1}$ in chloroform.

*Anal.* Calcd for $C_{31}H_{28}O_2PCo$: C, 71.26; H, 5.40. Found: C, 71.63; H, 5.72.

The nmr spectrum of the product in $DCCl_3$ was rather poorly resolved, probably because of paramagnetic impurities. Bands were observed at 60 Mc at −439 (aromatic protons), −191 (methylene group next to phenyl group), and −100 cps (methyl group), with smaller peaks also visible from the π-allylic hydrogens.

**Dicarbonyltriphenylphosphine-1-acetyl-2-methyl-π-allylcobalt from Chloro-1-acetyl-2-methyl-π-allylpalladium Dimer.** A mixture of 0.48 g (1 mmole) of chloro-1-acetyl-2-methyl-π-allylpalladium dimer[4] and 35 ml of 0.07 *M* $NaCo(CO)_4$ in ether[9] was stirred under nitrogen at room temperature for 1 hr. The black precipitate of palladium metal was removed by centrifuging, and the clear, orange solution (26 ml) was transferred by means of a hypodermic syringe to a carbon monoxide filled gasometric apparatus thermostated at 0°. To the solution was added 2.5 ml of 1.0 *M* triphenylphosphine in ether at 0°. In 45 min 33 ml of gas was evolved. A calculation of the rate constant for the reaction gave as an average value for 10 points over about 5 half-lives $3.15 \pm 0.09 \times 10^{-3}$ sec$^{-1}$. This value is about what would have been expected on the basis of values obtained for related compounds.[12] Evaporation of the solvent in the reaction mixture under reduced pressure and two recrystallizations of the crude product from methylene chloride by adding pentane, at −80° under nitrogen, gave 0.33 g (35%) of orange crystals of the product. The complex was rather unstable at room temperature and oxidized in air. The material, mp 153–155° dec, had infrared bands in chloroform solution at 1650, 1945, 2000, and 2070 cm$^{-1}$.

*Anal.* Calcd for $C_{26}H_{24}O_3PCo$: C, 65.83; H, 5.10. Found: C, 66.58; H, 5.60.

**Tetracarbonylcobaltotriphenylphosphine-1,1,2-trimethyl-π-allylpalladium.** A mixture of 0.63 g (1.5 mmoles) of chloro-1,1,2-trimethyl-π-allylpalladium dimer[3] and 45 ml of 0.07 *M* $NaCo(CO)_4$ in ether[9] was stirred under nitrogen at room temperature for 2 hr. Then 3.5 ml of 1.0 *M* triphenylphosphine in ether was added, and stirring was continued for another hour. The solvent was removed under reduced pressure, and the product was extracted from the residue with methylene chloride. The methylene chloride extracts were concentrated to a few milliliters and diluted with several volumes of pentane. Cooling in Dry Ice produced red-brown crystals of the product. Another recrystallization in the same manner gave 0.12 g (6.5%) of product, mp 117–120° dec, with infrared carbonyl absorptions in chloroform at 1875, 1910, 1950, and 2025 cm$^{-1}$.

*Anal.* Calcd for $C_{28}H_{26}O_4PCoPd$: C, 53.99; H, 4.21; P, 4.97. Found: C, 53.98; H, 4.35; P, 4.27.

**Chloro-π-allylpalladium Dimer from Tricarbonyl-π-allylcobalt.** To a solution of 60 ml of 0.07 *M* $Na\,Co(CO)_4$ in ether[9] was added 4.5 ml of 1.0 *M* allyl chloride in ether under nitrogen. The solution was stirred at room temperature overnight. The solvent was then removed under reduced pressure at 0°, and the remaining tricarbonyl-π-allylcobalt was redissolved in 20 ml of acetonitrile at 0°. Thirty milliters of 0.1 *M* $LiPdCl_3$ in acetonitrile[13] was added, and the mixture was stirred at room temperature overnight. The entire solution was poured onto a column of alumina and chromatographed. The yellow product was eluted with 1% methanol in methylene chloride. Evaporation of the solvent under reduced pressure and recrystallization from methylene chloride–pentane gave 0.166 g (22%) of yellow prisms, mp 152–155° dec (lit.[14] 145° dec).

*Anal.* Calcd for $C_6H_{10}Cl_2Pd_2$: C, 19.70; H, 2.76; Cl, 19.38. Found: C, 19.82; H, 2.86; Cl, 20.16.

**Chloro-1,3-dimethyl-π-allylpalladium Dimer from Tricarbonyl-1,3-dimethyl-π-allylcobalt.** This reaction was carried out as in the preceding example using 2-chloro-3-pentene in place of allyl chloride. There was obtained after purification by chromatography and recrystallization from methylene chloride by adding pentane, 0.13 g (16%) of yellow plates, mp 186–190° dec.

*Anal.* Calcd for $C_{10}H_{18}Cl_2Pd_2$: C, 28.46; H, 4.30. Found: C, 29.16; H, 4.79.

Another recrystallization from ethanol raised the melting point to 195–198° dec. The nmr spectrum of this product in deuteriochloroform at 60 Mc showed bands at −77.5 (doublet, $J_{ab}$ = 6.5 cps with relative area of 6), −221 (pair of quartets of relative area 2 with $J_{bc}$ = 11 cps), and −312 cps (a triplet with relative area 1).

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[12] R. F. Heck, *J. Am. Chem. Soc.*, **85**, 655 (1963).

[13] Only 1 mole of LiCl dissolves per mole of $PdCl_2$ in acetonitrile solution. Presumably $LiPdCl_3CH_3CN$ is formed.

[14] J. Smidt and W. Hafner, *Angew. Chem.*, 71, 284 (1959).

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# Nucleophilic Reactivity Constants toward Methyl Iodide and *trans*-[Pt(py)$_2$Cl$_2$]

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*Contribution from the Department of Chemistry, Northwestern University, Evanston, Illinois.* *Received August 11, 1967*

**Abstract:** The rates of reaction of a number of nucleophiles with methyl iodide and *trans*-[Pt(py)$_2$Cl$_2$] have been measured in methyl alcohol at 25°. Relative nucleophilic reactivity parameters, $n_{CH_3I}$ and $n_{Pt}$, have been calculated. It was not found possible to correlate these numbers with each other or with other extra-kinetic data. Equations in the literature for predicting nucleophilic reactivity have only a limited range of usefulness.

The subject of nucleophilic reactivity continues to be of great interest. A number of recent reviews and discussions have appeared.[3] There are also several semiempirical equations which attempt to predict and correlate rate data of reactions presumed to occur by bimolecular nucleophilic displacement (SN2) mechanisms.[4] In particular, it has been of interest to try to relate rate constants to extra-kinetic properties such as redox potentials.[5]

A practical difficulty has been the lack of extensive data for a large number of nucleophiles reacting with

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[1] Predoctoral fellow, National Institutes of Health, 1966–1968.

[2] Supported by the Royal Norwegian Council for Scientific and Industrial Research.

[3] J. O. Edwards and R. G. Pearson, *J. Am. Chem. Soc.*, **84**, 16 (1962); R. F. Hudson, *Chimia* (Aarau), 16, 173 (1962); J. F. Bunnett, *Ann. Rev. Phys. Chem.*, **14**, 271 (1963); J. Miller, *J. Am. Chem. Soc.*, **85**, 1628 (1963).

[4] These equations are reviewed by K. M. Ibne-Rasa, *J. Chem. Educ.*, **44**, 89 (1967).

[5] J. O. Edwards, *J. Am. Chem. Soc.*, 76, 1540 (1954).

several substrates in a fixed environment. A limited amount of data is available for reactions of methyl bromide and several other organic substrates in water.[6] In this work we report the second-order rate constants for a large number of nucleophiles reacting with methyl iodide and *trans*-[Pt(py)$_2$Cl$_2$] in methanol at 25°.

$$CH_3I + Y^- \xrightarrow{k_2} CH_3Y + I^- \qquad (1)$$

$$Pt(py)_2Cl_2 + Y^- \xrightarrow{k_2} Pt(py)_2ClY + Cl^-$$

$$Pt(py)_2ClY + Y^- \xrightarrow{\text{fast}} Pt(py)_2Y_2 + Cl^- \qquad (2)$$

The solvent was selected because of the solubility characteristics of the substrates and the nucleophiles. In addition a great deal of data has already been reported in this solvent for the platinum complex.[7] It is well known that the solvent plays a major role, not only in the magnitude of rate constants, but also in orders of nucleophilic reactivity.[8] Nevertheless, thanks to the work of Parker[8] and others, the probable effect of various solvents on nucleophiles of different types can be estimated. This means that rate data in other solvents can often be converted to approximate rate data in methanol for comparison.

Methyl iodide is selected as an example of a moderately soft electrophilic center and Pt(py)$_2$Cl$_2$ as an example of a very soft electrophilic center.[9] The characteristic of a soft electrophilic center is that it reacts rapidly with highly polarizable, or soft, nucleophiles. Proton basicity of the nucleophile is usually not important. Proton transfers are examples of reactions of hard electrophilic centers. In this case the best nucleophiles are hard bases such as $OH^-$ and $F^-$. Soft bases will be effective only if they are also strong bases toward the proton, such as $S^{2-}$. For proton transfers, a Brønsted relationship usually exists between the rate constants and the p$K_a$ of a series of bases.[10]

The p$K_a$ values of a number of acids are known in methanol.[11] Again it is possible to roughly estimate the p$K_a$ in methanol from a known p$K_a$ in water. Charge on the conjugate acid is very important. Thus

$$HB \rightleftharpoons B^- + H^+ \qquad (3)$$

$$HB^+ \rightleftharpoons B + H^+ \qquad (4)$$

The p$K_a$ for reaction 3 usually increases by about four units in going from water to methanol, whereas reaction 4 is much less affected. In other words, it is more difficult to form ions from neutral molecules in methanol than in water.

The data obtained in this paper and other data from the literature are converted into nucleophilic reactivity constants, $n_{CH_3I}$ and $n_{Pt}$, which are defined as logarithms of the ratios of the second-order rate constants of the nucleophile divided by the second-order rate constant for solvolysis in methanol.[6,7] Thus, for a nucleophile Y

$$n_{Pt} = \log (k_Y/k_{CH_3OH})$$

$$n_{CH_3I} = \log (k_Y/k_{CH_3OH})$$

These $n_{Pt}$ values differ from those in ref 7 in that the first-order rate constant for solvolysis has now been divided by 26 moles/l. to obtain $k_S$. This agrees with the recent definition of $n^0_{Pt}$ by Belluco, *et al.*[12] However, since Swain and Scott used this same convention in their original work[6] defining $n_{CH_3Br}$, we have dropped the superscript zero. The $n$ values calculated in this work are at 25°, whereas earlier[7] $n_{Pt}$ values are at 30°. We will assume that the change with temperature is small over this range.

## Experimental Section

**Preparation and Purification of Reagents.** Baker Analyzed methyl iodide was washed with potassium carbonate solution and then several times with water. The methyl iodide was then carefully dried over magnesium sulfate and distilled from silver wool. The purified compound was stored over silver wool under nitrogen in a flask that was painted black. This purification procedure was repeated approximately once a month.

*trans*-[Pt(py)$_2$Cl$_2$] was prepared according to the method of Kauffman.[13]

Baker Analyzed methanol was refluxed for at least 5 hr with magnesium methoxide and distilled under nitrogen free from moisture and carbon dioxide. The first 15% of distillate was discarded. The purified product was stored under nitrogen and used for the methyl iodide experiments. Oxygen-free water was added to the methanol when inorganic salts were insufficiently soluble in pure methanol. The purified methanol was also used for those reactions of the platinum complex with oxygen-sensitive or water-sensitive nucleophiles, but for most reactions of this complex, Baker Analyzed methanol was used without further purification.

Inorganic salts and thiourea were recrystallized from water and dried *in vacuo* if not of analytical grade.

Amines of the highest purity available were purified by recrystallizing their quaternized salts. The amines were then distilled twice from sodium hydroxide pellets through a 12-plate column with controlled temperature. All other liquid nucleophiles were purified in this way; a central cut of distillate was used for the kinetic measurements.

Anhydrous hydroxylamine was made according to the method of Bissot, *et al.*[14] Anhydrous hydrazine was prepared according to the method of Beckman;[15] the final product contained about 1% ammonia and less than 0.5% water, as determined by titration with HCl and KIO$_3$. Anhydrous ammonia was used without further purification, as was cylinder carbon monoxide. Imidazole was Eastman product frozen out from water–alcohol mixtures twice and then recrystallized from benzene.

The nucleophile $((C_2H_5)_2N)_3P$ was prepared according to the method of Burgada.[16] The distilled product was washed with ice-cold water, dissolved in pentane, dried, and finally distilled twice, bp 62–63° (2 mm). Because of its rapid reaction with methanol, this compound was studied kinetically in acetonitrile solution. Several other neutral nucleophiles were studied in both methanol

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(6) C. S. Swain and C. B. Scott, *J. Am. Chem. Soc.*, **75**, 141 (1953).

(7) U. Belluco, L. Cattalini, F. Basolo, R. G. Pearson, and A. Turco, *ibid.*, **87**, 241 (1965).

(8) (a) A. J. Parker, *Quart. Rev.* (London), **14**, 163 (1962); (b) A. J. Parker, *et al.*, *J. Am. Chem. Soc.*, **88**, 1911 (1966); (c) *J. Chem. Soc., Sect. B*, 152 (1962).

(9) R. G. Pearson, *J. Am. Chem. Soc.*, **85**, 3533 (1963); *Science*, **151**, 172 (1966).

(10) However, negative deviations will occur for soft bases compared to hard bases of the same p$K_a$: M. Eigen, *Angew. Chem. Intern. Ed. Engl.*, **3**, 1 (1964).

(11) See ref 8b and E. Grunwald and E. Price, *J. Am. Chem. Soc.*, **86**, 4517 (1964), for data and earlier references.

(12) U. Belluco, M. Martelli, and A. Orio, *Inorg. Chem.*, **5**, 582 (1966).

(13) G. G. Kauffman, *Inorg. Syn.*, **7**, 251 (1963).

(14) T. C. Bissot, *et al.*, *J. Am. Chem. Soc.*, **79**, 796 (1957).

(15) R. R. Wenner and A. O. Beckman, *ibid.*, **54**, 2787 (1932).

(16) R. Burgada, *Ann. Chim.*, **8**, 347 (1963).

and acetonitrile solutions to set up reactivity ratios for interconversion of data. The conductivity method was always used in acetonitrile.

Alkylarsines and -phosphines were made from the appropriate Grignard reagents and phosphorus or arsenic trichloride. After the HCl adducts in 6 *M* HCl were washed several times with ether to remove by-products, the compounds were finally liberated with sodium hydroxide pellets, distilled under nitrogen or, if necessary, *in vacuo*. Commercial triphenylphosphine and triphenylarsine were recrystallized twice from methanol.

The sulfides were commercial products distilled over metallic sodium in nitrogen. The selenides were made by the method of Bird and Challenger;[17] dimethyl selenide was distilled under nitrogen after being dried over sodium. Dibenzyl selenide was recrystallized twice from lukewarm absolute methanol prior to use.

Baker Analyzed phenol was used without further purification. Eastman thiophenol and selenophenol were distilled in a nitrogen atmosphere prior to use. Trimethyl phosphite in ether solution was treated with sodium metal, filtered, and then distilled. Triphenylsilanol was recrystallized twice from benzene.

Tetraethylammonium trichlorostannite was prepared according to the method of Parshall[18] by adding together equimolar quantities of tetraethylammonium chloride and stannous chloride in 0.5 *M* hydrochloric acid solution. The compound was recrystallized twice from absolute ethanol and washed with cold absolute ethanol, in which the product is nearly insoluble. All operations were performed under nitrogen. The concentration of tin(II) was found to be from 97 to 98% of the expected concentration by titration with thiosulfate after the addition of excess potassium triiodide. This salt was used in the methyl iodide experiments. For the experiments with the platinum complex, where excess chloride ions would not complicate the kinetics, the trichlorostannite ion was prepared by adding concentrated hydrochloric acid to methanol solutions of stannous chloride.

**Kinetics.** All rate constant determinations were performed at 25°. The rates of many of the reactions of methyl iodide and of the platinum complex with neutral nucleophiles were measured by following the change in electrical conductivity at 1000 cps with an Industrial Instruments Model RC16B1 conductivity meter. The electrodes of the conductivity cells were of platinum; those cells used for the reactions of methyl iodide were painted black to avoid photoinitiated side reactions. For the experiments with methyl iodide, the conductometric method was used only for reactions under pseudo-first-order conditions; the concentrations of nucleophiles ranged from 0.04 to 0.15 *M* and were at least 80 times greater than the concentration of methyl iodide. For each nucleophile, at least three different concentrations were used. The measurements were performed under nitrogen when necessary.

In the experiments with the Pt(II) complex, the concentration of the platinum compound was always $5 \times 10^{-5}$ *M* and the concentration of nucleophile ranged from $1 \times 10^{-3}$ to $1 \times 10^{-1}$ *M*, depending upon reactivity, except for the case of the phosphines, where the concentration of the platinum complex was $2.5 \times 10^{-5}$ *M* and the phosphine concentration was $5 \times 10^{-5}$ *M*. The rates of reaction of *trans*-$[Pt(py)_2Cl_2]$ with all of the ionic nucleophiles and with some of the neutral nucleophiles were measured by following the change with time of optical density at some selected wavelength in the ultraviolet region by means of a Cary 14 spectrophotometer.

Second-order conditions were used for those reactions of methyl iodide that were too slow for pseudo-first-order conditions, and for reactions with ionic nucleophiles. The rate constants for nonionic nucleophiles obtained from pseudo-first-order kinetic runs were checked by second-order kinetics, and the rate constants were calculated from the first 5 to 10% reacted. The discrepancy was never greater than 3%. The concentrations of nucleophiles and methyl iodide were in the range of 0.02–0.08 *M*, depending upon the reactivity. After appropriate time intervals, 5- or 10-ml aliquots were withdrawn from the reaction vessel and added to 30 ml of water and 15 ml of benzene, ice-cold if necessary, in a separatory funnel. The organic layer was washed repeatedly with water, and the combined water extracts were finally washed with low-boiling petroleum ether to remove traces of benzene, which was found to make the end point in the following titration diffuse.

The determination of iodide ion was performed with silver nitrate and eosin indicator. The accuracy of this method was better than 0.2% with 0.05 *M* silver nitrate titrant and was approximately 0.5% for 0.01 *M* silver nitrate. The loss of iodide ions during the removal of unreacted methyl iodide was found to be less than 0.5% and was therefore neglected. In each run, five to nine determinations of iodide ion were performed. The second-order rate constants were calculated from the first 70% reacted.

The rate constants for hydroxylamine, ammonia, and hydrazine were calculated from the first 10 to 20% reacted in the presence of 10 to 20% of the corresponding hydrochlorides in a concentration of 0.05 *M*. In the case of hydrazine a very small amount of water, 1% by volume, was added because of the low solubility of hydrazine hydrochloride in methanol.

The reaction between cyanide ion and methyl iodide was followed by determining cyanide ion by the Liebig–Deniges method.[19] Thiocyanate ions in the presence of iodide ions were determined by potentiometric titration with silver nitrate, using a Radiometer titration assembly with a Type PK499 mercury–mercurous sulfate electrode.

The reaction between sulfite ion and methyl iodide was followed by adding aliquots of the reaction mixture to excess iodine solution and titrating back with thiosulfate. In all runs sodium methoxide was added in concentrations exceeding that of the sulfite ion. All operations were performed under nitrogen. The reaction with thiosulfate was followed in the same way. Both reactions were run in an 80% methanol–20% water mixture (v/v) because of the low solubility of these salts in methanol.

The reaction between trimethyl phosphite and methyl iodide was followed by measuring the formation of the product, dimethyl methylphosphonate, by its phosphoryl absorbance[20] using a Perkin-Elmer Model 337 infrared spectrophotometer and barium fluoride cells. Because of difficulties in getting a stable base line, this value is not very accurate. Extreme care was taken during these runs to exclude moisture. Rates are initial values only.

The reaction between tetraethylammonium trichlorostannite and methyl iodide in the presence of HCl was followed by determination of liberated iodide ions. As the rate of formation of iodide ions was only a little higher than that from pure solvolysis, the rate constants will necessarily be rather inaccurate.

The rates of formation of chloride ions from *trans*-$[Pt(py)_2Cl_2]$ and of iodide ions from methyl iodide from the reaction of methanol saturated with carbon monoxide were found to be similar to the rate of pure solvolysis. (The concentration of carbon monoxide in a saturated methanolic solution at 25° is $8.0 \times 10^{-3}$ *M*.[21]) Allyl alcohol gave a similar result. The same result was obtained for the reaction of methyl iodide with triphenylstibine and for the reaction of $Pt(py)_2Cl_2$ with 0.04 *M* fluoride ion.

Solutions of the sodium salts of dimethyl phosphite, triphenylsilanol, and phenol were made by adding a 30 to 100% excess of the acids to solutions of sodium methoxide of known molarity. Solu-

**Table I**

| Product | | Calcd, % | Found, % |
|---|---|---|---|
| $[Pt(py)_2(P(C_6H_5)_3)_2](OTs)_2$ | Pt | 16.0 | 15.6 |
| | C | 59.0 | 58.0 |
| | H | 4.45 | 4.51 |
| | N | 2.29 | 2.19 |
| $[Pt(py)_2(S(benz)_2)_2](OTs)_2$ | Pt | 17.3 | 17.7 |
| | C | 55.4 | 54.2 |
| | H | 4.65 | 4.71 |
| | N | 2.49 | 2.48 |
| $[Pt(py)_2(Se(benz)_2)_2](OTs)_2$ | Pt | 16.0 | 16.4 |
| | C | 51.3 | 49.8 |
| | H | 4.30 | 4.19 |
| | N | 2.30 | 2.53 |
| $[Pt(py)_2(imid)_2]Cl_2$ | C | 34.30 | 33.3 |
| | H | 3.24 | 3.32 |
| | N | 14.99 | 14.9 |
| $[Pt(py)_2(As(C_6H_5)_3)_2](OTs)_2$ | Pt | 14.9 | 14.9 |
| | C | 55.1 | 53.4 |
| | H | 4.16 | 4.04 |
| | N | 2.14 | 1.97 |

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(17) M. L. Bird and F. Challenger, *J. Chem. Soc.*, 571 (1942).

(18) G. W. Parshall, private communication.

(19) I. M. Kolthoff and E. B. Sandell, "Textbook of Quantitative Analysis," 3rd ed, The Macmillan Co., New York, N. Y., 1952, p 546.

(20) G. Aksnes and D. Aksnes, *Acta Chem. Scand.*, **18**, 38 (1964).

(21) G. Just, *Z. Physik. Chem.*, 37, 342 (1901).

**Table II.** Rate Constants in Methanol at 25°

| | Nucleophile | $10^3k_2$, $M^{-1}$ sec$^{-1}$ | |
|---|---|---|---|
| | | *trans*-[Pt(py)$_2$Cl$_2$] | $CH_3I$ |
| 1. | $CH_3OH$ | 0.00027 | 0.00000013[b] |
| 2. | $CH_3O^-$ | Very slow[a] | 0.251[c] |
| 3. | $F^-$ | Very slow | 0.00005[d] |
| 4. | $Cl^-$ | 0.45[a] | 0.0030[e] |
| 5. | $NH_3$ | 0.47[a] | 0.041 |
| 6. | $C_5H_5N$ | 0.55[a] | 0.022[f] |
| 7. | $NO_2^-$ | 0.68[a] | 0.029 |
| 8. | $(C_6H_5CH_2)_2S$ | 0.80 | 0.009 |
| 9. | $N_3^-$ | 1.55[a] | 0.078[e] |
| 10. | $NH_2OH$ | 2.9[a] | 0.50 |
| 11. | $H_2NNH_2$ | 2.93[a] | 0.51 |
| 12. | $C_6H_5SH$ | 5.7[a] | 0.064 |
| 13. | $Br^-$ | 3.7[a] | 0.0798[g] |
| 14. | $(C_2H_5)_2S$ | 9.85 | 0.0282[h] |
| 15. | $(CH_3)_2S$ | 21.9 | 0.0452 |
| 16. | $(CH_3O)_2PO^-$ | 30.4 | 1.28 |
| 17. | $(CH_2)_5S$ | 30.7 | 0.0342 |
| 18. | $(CH_2)_4S$ | 40.9 | 0.0587 |
| 19. | $SnCl_3^-$ | 70 | 0.0009 |
| 20. | $(C_6H_5CH_2)_2Se$ | 101 | 0.022[i] |
| 21. | $I^-$ | 107[a] | 3.42[j] |
| 22. | $(CH_3)_2Se$ | 148 | 0.268 |
| 23. | $SCN^-$ | 180[a] | 0.574 |
| 24. | $SO_3^{2-}$ | 250[a] | 44.5 |
| 25. | $C_6H_{11}NC$ | 640 | Very slow |
| 26. | $(C_6H_5)_3Sb$ | 1,810 | Very slow |
| 27. | $(C_6H_5)_3As$ | 2,320 | 0.0075 |
| 28. | $CN^-$ | 4,000 | 0.645 |
| 29. | $(CH_3O)_3P$ | 4,890 | 0.02 |
| 30. | $SeCN^-$ | 5,150[a] | 9.13[k] |
| 31. | $C_6H_5S^-$ | 6,000[a] | 1070 |
| 32. | $SC(NH_2)_2$ | 6,000[a] | 2.41 |
| 33. | $S_2O_3^{2-}$ | 9,000[a] | 114 |
| 34. | $(C_2H_5)_3As$ | 14,100 | 1.03 |
| 35. | $(C_6H_5)_3P$ | 249,000 | 1.29 |
| 36. | $(C_4H_9)_3P$ | 272,000 | 63 |
| 37. | $(C_2H_5)_3P$ | 290,000 | 66 |
| 38. | $CH_3COO^-$ | Very slow[o] | 0.0027[l] |
| 39. | $C_6H_5COO^-$ | ... | 0.002[l] |
| 40. | $C_6H_5O^-$ | ... | 0.073[l] |
| 41. | CO | Very slow | Very slow |
| 42. | $C_6H_5NH_2$ | 0.43 | 0.052 |
| 43. | $C_6H_5N(CH_3)_2$ | ... | 0.0562[m] |
| 44. | 2,6-Dimethylpyridine | ... | 0.00042[f] |
| 45. | $\alpha$-Picoline | 0.05 | 0.0065[f] |
| 46. | Pyrrolidine | ... | 2.2 |
| 47. | Piperidine | 0.38 | 2.6 |
| 48. | N,N-Dimethyl-cyclohexylamine | ... | 0.692[n] |
| 49. | $(C_2H_5)_2NH$ | ... | 1.2[p] |
| 50. | $(C_2H_5)_3N$ | Very slow | 0.595[f] |
| 51. | $C_6H_5Se^-$ | ... | 7000 |
| 52. | $(C_6H_5)_3SiO^-$ | ... | 0.19 |
| 53. | $C_6H_5SO_2NCl^-$ | ... | 8.22[q] |
| 54. | $C_6H_5SO_2NH^-$ | ... | 0.18[q] |
| 55. | Phthalimide anion | ... | 0.37[q] |
| 56. | $[(C_2H_5)_2N]_3P$ | 10[r] | 45.0[r] |
| 57. | Imidazole | 0.74 | 0.012 |
| 58. | Allyl alcohol | Very slow | Very slow |

[a] U. Belluco, L. Cattalini, F. Basolo, R. G. Pearson, and A. Turco, *J. Am. Chem. Soc.*, **87**, 241 (1965). These data are at 30°. [b] The first-order rate constant for solvolysis is $3.3 \times 10^{-9}$. A. J. Parker, *J. Chem. Soc.*, 1328 (1961), gives the value $4 \times 10^{-9}$, calculated from rate at 59.8°. [c] I. K. Alet and B. D. England, *J. Chem. Soc.*, 5259 (1961), give the value $2.55 \times 10^{-4}$ sec$^{-1}$. [d] This value is calculated by using a relation between reactivities in methanol and water given by R. H. Bathgate and E. A. Moelwyn-Hughes, *ibid.*, 2642 (1959). [e] A J. Parker, *ibid.*, 1328 (1961) (25.1°). [f] N. Tokura and Y. Kondo, *Bull. Chem. Soc. Japan*, **37**, 133 (1964), give data from which the value $2.13 \times 10^{-5}$ was calculated for pyridine. The values in the table for triethylamine, $\alpha$-picoline, and 2,6-dimethylpyridine are from this same reference. [g] E. A. Moelwyn-Hughes, *J. Chem. Soc.*, 838 (1952). [h] The value $2.97 \times 10^{-5}$ was calculated from the data of Y. K. Syrkin and I. T. Gladishev, *Acta Physicochim. USSR*, **2**, 291 (1935). [i] Since the product $(C_6H_5CH_2)_2SeCH_3^+$ is not stable, the rate constant was first estimated from the first 5% reacted in a pseudo-first-order run, assuming that the equivalent conductance for this ion is the same as that for the corresponding sulfonium ion. Then the rate constant was calculated from the first 5% reacted in a second-order run by titration of the liberated iodide ions. The agreement between the two runs was 3%. [j] P. Beronius, *Acta Chem. Scand.*, **14**, 1151 (1961). [k] A. J. Parker, *J. Chem. Soc.*, 4398 (1961). [l] D. Cook, I. P. Evans, E. C. E. Ko, and A. J. Parker, *ibid.*, *Sect. B*, 404 (1966). [m] D. P. Evans, *ibid.*, 422 (1944). This reference gives rate constants for other anilines. [n] E. R. A. Peeling and B. D. Stone, *Chem. Ind.* (London), 1625 (1959). [o] S. P. Tanner, F. Basolo, and R. G. Pearson, *Inorg. Chem.*, **6**, 1089 (1967). [p] From results in acetonitrile and a rate ratio $k_{CH_3CN}/k_{CH_3OH} = 122$ found for piperidine. [q] J. H. Beale, Ph.D. Thesis, Brown University, 1966. [r] From acetonitrile data and rate ratios of $k_{CH_3CN}/k_{CH_3OH} = 4.3$ found for $(C_6H_5)_3P$ reacting with $CH_3I$, and $k_{CH_3CN}/k_{CH_3OH} = 2$ for pyridine reacting with $Pt(py)_2Cl_2$.

tions of sodium thiophenoxide and selenophenoxide were made similarly. The reaction rates of these two nucleophiles were determined by ultraviolet spectrophotometry. Cell compartments and solutions were carefully flushed with nitrogen. From more concentrated runs the desired sulfide and selenide were obtained in greater than 90% yield.

The reaction of methyl iodide with sodium triphenylsilanolate was followed by titrating the liberated iodide ions. The expected product ($(C_6H_5)_3SiOCH_3$) was obtained in greater than 80% yield, showing that the formation of $[(C_6H_5)_3Si]_2O$ can be neglected. This is consistent with the findings of Grubb, who found the formation of $[(C_6H_5)_3Si]_2O$ to be a slow reaction in methanol.[22]

The reactions of the amines with $Pt(py)_2Cl_2$ are complicated by some formation of *trans*-$Pt(py)_2(OCH_3)_2$. This causes an error in rates determined by the conductometric method. Accordingly rates for pyridine, piperidine, and ammonia were also checked by ultraviolet in the 320–340-m$\mu$ region. The compounds *trans*-$[Pt(py)_2(pip)_2]Cl_2$, *trans*-$[Pt(py)_2(NH_3)_2]Cl_2$, and $[Pt(py)_4]Cl_2$ were synthesized and their spectra checked in the region of interest. The species $[Pt(py)_2(OCH_3)_2]$ (*trans*?) was made from *trans*-$[Pt(py)_2I_2]$ and $NaOCH_3$, but not isolated. Its spectrum showed $\epsilon$ 4500 at 290 m$\mu$, and $\epsilon$ 3920 at 300 m$\mu$. The reactions of $CH_3I$ in buffered solutions of amines are not much affected because the amine rate is much greater than the solvolysis rate, unlike the platinum case.

In a number of other cases the expected products of reaction of the platinum complex with the nucleophiles were synthesized by larger scale runs in methanol using equivalent concentrations. Silver tosylate was added to precipitate silver chloride. After filtration, the filtrate was evaporated to dryness. The product was washed with water and with ether and then recrystallized from ether–methanol. Analyses are given in Table I.

In the case of $((C_2H_5)_2N)_3P$ reacting with $[Pt(py)_2Cl_2]$, a crystalline product was not obtained. A glassy, hygroscopic material was formed whose infrared spectrum suggested that it was the expected $[Pt(py)_2(P(NR_2)_3)_2]^{2+}$. In the case of $CH_3I$ the product was assumed to be $((C_2H_5)_2N)_3PCH_3^+$ by analogy with other reactions of alkyl halides.[23]

The products in the case of $SnCl_3^-$ as a nucleophile were not isolable. From the literature they were expected to be $CH_3SnCl_3$[24] and *trans*-$[Pt(py)_2(SnCl_3)_2]$.[25]

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(22) W. T. Grubb, *J. Am. Chem. Soc.*, **76**, 3408 (1954).

(23) H. Nöth and H. J. Vetter, *Ber.*, **94**, 1505 (1961).

(24) A. Tschakirian, *et al.*, *Compt. Rend.*, **202**, 138 (1936); R. W. Leeper, *Iowa State Coll. J. Sci.*, **18**, 57 (1943).

(25) R. D. Cramer, *et al.*, *J. Am. Chem. Soc.*, **85**, 1691 (1963); A. G. Davies, *et al.*, *ibid.*, **85**, 1692 (1963).

## Results

Whereas the rates of reaction of methyl iodide usually follow the simple second-order rate law

$$\text{rate} = k_2[\text{CH}_3\text{I}][\text{Y}] \tag{5}$$

the rates for *trans*-[Pt(py)$_2$Cl$_2$] follow the two-term rate law that is well known for substitution reactions of platinum(II) complexes.[26]

$$\text{rate} = k_1[\text{complex}] + k_2[\text{complex}][\text{Y}] \tag{6}$$

The rate constant $k_1$ is for the solvent path, and $k_2$ is for the direct reagent path. For the substitution reactions with *trans*-[Pt(py)$_2$Cl$_2$], an excess of nucleophile was used, and the pseudo-first-order rate constants $k_{\text{obsd}}$ were determined. The experimental $k_{\text{obsd}}$ is related to $k_1$ and $k_2$ by

$$k_{\text{obsd}} = k_1 + k_2[\text{Y}] \tag{7}$$

For each reaction, the values of $k_{\text{obsd}}$ were determined at five or more different concentrations of nucleophile, Y. Linear plots of $k_{\text{obsd}}$ *vs.* Y were obtained; the extrapolated value of $k_{\text{obsd}}$ at zero Y is $k_1$, and the slope is $k_2$. These values are given in Table II, along with the values of $k_2$ for the reactions of methyl iodide. A number of values from the literature are also included. Some of these are only estimated, but they are so marked. Table III gives values of $n_{\text{Pt}}$ and $n_{\text{CH}_3\text{I}}$ along with values of $E_n$, p$K_a$ in H$_2$O, and p$K_{\text{CH}_3\text{Hg}^+}$. The latter quantity refers to the equilibrium, in aqueous solution at 25°

$$\text{CH}_3\text{HgY} \rightleftharpoons \text{CH}_3\text{Hg}^+ + \text{Y}^- \tag{8}$$

Since the methylmercury cation is a very soft Lewis acid, it might be a more suitable reference than the proton, which is hard.

## Discussion

Figure 1 shows that there is little correlation between $n_{\text{Pt}}$ and $n_{\text{CH}_3\text{I}}$. This is not too surprising since Pt(II) is a much softer electrophilic center than is carbon in methyl iodide. It can be seen that, in general, the most polarizable reagents lie above the line in Figure 1; that is, they react relatively faster with Pt(II). The straight line in Figure 1 has no significance except that of dividing the nucleophiles into roughly two groups. The least polarizable reagents then lie below the line, reacting relatively slower with Pt(II). Above the line are found bases in which the donor atom is P, As, Se, C, and Sn. Below the line are O and N donor atom bases, as well as F$^-$.

Surprisingly, I$^-$ is below the line. However, there is a marked tendency for anionic bases to lie below the line in general. Presumably this is explained by postulating that, in the transition state, the carbon atom of CH$_3$I has developed a greater positive charge than has platinum in Pt(py)$_2$Cl$_2$. This is not unreasonable in view of the probable mechanisms of the two substitution reactions. That is, for CH$_3$I there is substantial bond breaking in the transition state, whereas for Pt(II) there is very little bond breaking, a five-coordinated intermediate being formed.[26,27]

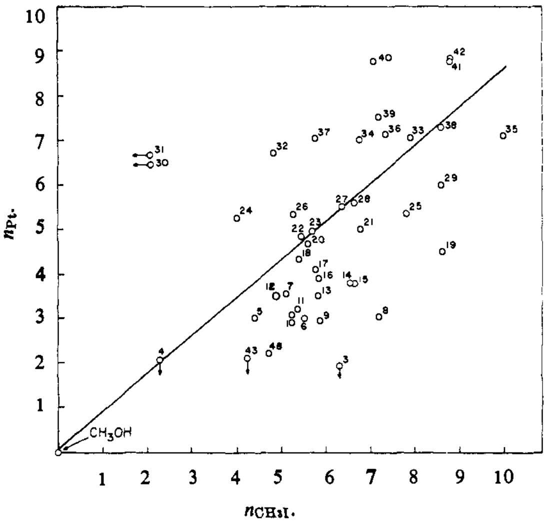

Figure 1. Plot of $n_{\text{Pt}}$ against $n_{\text{CH}_3\text{I}}$. The numbers refer to the nucleophiles as listed in Table III.

The mechanism for Pt(II) substitution resembles more closely that for aromatic substitution, rather than aliphatic substitution. Miller[28] has developed a theory for predicting rates of aromatic substitutions. A typical reactivity sequence for nucleophiles in aromatic substitution is found experimentally and theoretically to be C$_6$H$_5$S$^-$ $\gg$ CH$_3$O$^-$ > N$_3^-$ $\gg$ SCN$^-$ > I$^-$ > Br$^-$ > Cl$^-$ > F$^-$. This is very poor with respect to CH$_3$O$^-$ and N$_3^-$ as far as Pt(II) substitution is concerned.

Unfortunately, it is rather difficult to use Miller's method to predict reactivities for other nucleophiles since bond energies, ionization potentials, and solvation energies are needed, as well as reorganization energies on forming the transition state. The theory is quite similar to that of Hudson,[29] who uses the same properties but in a more flexible way (more parameters that can be varied). We have made a serious effort to estimate $n_{\text{CH}_3\text{I}}$ values using Hudson's method for about 15 of the nucleophiles listed in Table III, where bond energies, ionization potentials, and solvation energies were available or could be estimated. Even though three entirely adjustable parameters were allowed, the results were extremely poor. Lack of bond-energy data prevented the application of Hudson's method to the calculation of $n_{\text{Pt}}$, but there is little reason to believe that it would be more successful.

It can be seen from Figure 2 that there is no correlation between $n_{\text{Pt}}$ and the strength of the nucleophile as a proton base. The figures show p$K_a$ in water, but using the known or estimated p$K_a$ values in methanol would do little to improve the correlation. As explained

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(26) C. H. Langford and H. B. Gray, "Ligand Substitution Processes," W. A. Benjamin, Inc., New York, N. Y., 1965, Chapter 2.

(27) See F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, John Wiley and Sons, Inc., New York, N. Y., 1967, Chapter 5.

(28) J. Miller, *J. Am. Chem. Soc.*, 85, 1628 (1963); D. L. Hill, K. C. Ho, and J. Miller, *J. Chem. Soc., Sect. B*, 299 (1966).

(29) R. F. Hudson, *Chimia* (Aarau), 16, 173 (1962); "Structure and Mechanism in Organo-Phosphorus Chemistry," Academic Press Inc., New York, N. Y., 1965, Chapter 4.

**Table III.** Properties of Various Nucleophiles

| | Nucleophile | $n_{Pt}$ | $n_{CH_3I}$ | $E_n$[a] | $pK_a$ | $pK_{CH_3Hg^+}$[h] |
|---|---|---|---|---|---|---|
| 1. | $CH_3OH$ | 0.00 | 0.00 | 0 | −1.7[a] | —1.74 |
| 2. | CO | <2.0 | <2.0 | ... | ... | ... |
| 3. | $CH_3O^-$ | <2.4 | 6.29 | 1.65 | 15.7[a] | 9.42 |
| 4. | $F^-$ | <2.2 | ~2.7 | −0.27 | 3.45[b] | 1.50 |
| 5. | $Cl^-$ | 3.04 | 4.37 | 1.24 | (−5.7)[a] | 5.25 |
| 6. | $NH_3$ | 3.07 | 5.50 | 1.36 | 9.25[b] | 7.60 |
| 7. | Imidazole | 3.44 | 4.97 | ... | 7.10[c] | ... |
| 8. | Piperidine | 3.13 | 7.30 | ... | 11.21[c] | ... |
| 9. | Aniline | 3.16 | 5.70 | (1.78) | 4.58[c] | ... |
| 10. | Pyridine | 3.19 | 5.23 | (1.20) | 5.23[c] | 4.8 |
| 11. | $NO_2^-$ | 3.22 | 5.35 | 1.73 | 3.37[a] | (2.5) |
| 12. | $(C_6H_5CH_2)_2S$ | 3.43 | 4.84 | ... | ... | ... |
| 13. | $N_3^-$ | 3.58 | 5.78 | (1.58) | 4.74[a] | 6.0[i] |
| 14. | $NH_2OH$ | 3.85 | 6.60 | ... | 5.82[c] | ... |
| 15. | $NH_2NH_2$ | 3.86 | 6.61 | ... | 7.93[c] | ... |
| 16. | $C_6H_5SH$ | 4.15 | 5.70 | ... | ... | ... |
| 17. | $Br^-$ | 4.18 | 5.79 | 1.51 | (−7.7)[a] | 6.62 |
| 18. | $(C_2H_5)_2S$ | 4.52 | 5.34 | ... | ... | ... |
| 19. | $((C_2H_5)_2N)_3P$ | 4.54 | 8.54 | ... | ... | ... |
| 20. | $(CH_3)_2S$ | 4.87 | 5.54 | ... | −5.3[d] | ... |
| 21. | $(CH_3O)_2PO^-$ | 5.01 | 7.00 | ... | ... | ... |
| 22. | $(CH_2)_5S$ | 5.02 | 5.42 | ... | ... | ... |
| 23. | $(CH_2)_4S$ | 5.14 | 5.66 | ... | −4.8[d] | ... |
| 24. | $SnCl_3^-$ | 5.44 | ~3.84 | ... | ... | ... |
| 25. | $I^-$ | 5.46 | 7.42 | 2.06 | (−10.7)[a] | 8.60 |
| 26. | $(C_6H_5CH_2)_2Se$ | 5.53 | 5.23 | ... | ... | ... |
| 27. | $(CH_3)_2Se$ | 5.70 | 6.32 | ... | ... | ... |
| 28. | $SCN^-$ | 5.75 | 6.70 | 1.83 | (−0.7)[a] | 6.05 |
| 29. | $SO_3^{2-}$ | 5.79 | 8.53 | 2.57 | 7.26[a] | 8.11 |
| 30. | $C_6H_{11}NC$ | 6.34 | <2.0 | ... | ... | ... |
| 31. | $(C_6H_5)_3Sb$ | 6.79 | <2.0 | ... | ... | ... |
| 32. | $(C_6H_5)_3As$ | 6.89 | 4.77 | ... | ... | ... |
| 33. | $SeCN^-$ | 7.11 | 7.85 | ... | ... | ... |
| 34. | $CN^-$ | 7.14 | 6.70 | 2.79 | 9.3[b] | 14.1 |
| 35. | $C_6H_5S^-$ | 7.17 | 9.92 | (2.9) | 6.52[e] | ... |
| 36. | $SC(NH_2)_2$ | 7.17 | 7.27 | 2.18 | −0.96[f] | (7) |
| 37. | $(CH_3O)_3P$ | 7.23 | ~5.2 | ... | ... | ... |
| 38. | $S_2O_3^{2-}$ | 7.34 | 8.95 | 2.52 | 1.9[a] | 10.90 |
| 39. | $(C_2H_5)_3As$ | 7.68 | 6.90 | ... | <2.6[f] | ... |
| 40. | $(C_6H_5)_3P$ | 8.93 | 7.00 | ... | 2.73[g] | ... |
| 41. | $(n\text{-}C_4H_9)_3P$ | 8.96 | 8.69 | ... | 8.43[g] | ... |
| 42. | $(C_2H_5)_3P$ | 8.99 | 8.72 | ... | 8.69[g] | 15.0 |
| 43. | $CH_3COO^-$ | <2.0 | 4.3 | (0.95) | 4.75[f] | ... |
| 44. | $C_6H_5COO^-$ | ... | 4.5 | ... | 4.19[f] | ... |
| 45. | $C_6H_5O^-$ | ... | 5.75 | (1.46) | 9.89[f] | ... |
| 46. | $C_6H_5N(CH_3)_2$ | ... | 5.64 | ... | 5.06[f] | ... |
| 47. | 2,6-DMP[o] | ... | 3.51 | ... | ... | ... |
| 48. | α-Picoline | ~2.2 | 4.7 | ... | 6.48[f] | ... |
| 49. | Pyrrolidine | ... | 7.23 | ... | 11.27[j] | ... |
| 50. | N,N-DHA[o] | ... | 6.73 | ... | ... | ... |
| 51. | $(C_2H_5)_3N$ | ... | 6.66 | ... | 10.70[c] | ... |
| 52. | $(C_2H_5)_2NH$ | ... | ~7.0 | ... | 11.0[c] | ... |
| 53. | $C_6H_5Se^-$ | ... | ~10.7 | ... | ... | ... |
| 54. | $(C_6H_5)_3SiO^-$ | ... | 6.2 | ... | ... | ... |
| 55. | $C_6H_5SO_2NCl^-$ | ... | 6.8 | ... | (3.0)[n] | ... |
| 56. | $C_6H_5SO_2NH^-$ | ... | 5.1 | ... | (8.5)[n] | ... |
| 57. | Phthalimide anion | ... | 5.4 | ... | 7.4[n] | ... |
| 58. | $HS^-$ | ... | (8)[k] | 2.10 | 7.8[a] | (16) |
| 59. | $SO_4^{2-}$ | ... | (3.5)[k] | 0.59 | 2.0[a] | (1.5) |
| 60. | $NO_3^-$ | ... | (1.5)[k] | (0.29) | −1.3[a] | ... |
| 61. | $(C_6H_5)_3Ge^-$ | ... | (12)[l] | ... | ... | ... |
| 62. | $(C_6H_5)_3Sn^-$ | ... | (11.5)[l] | ... | ... | ... |
| 63. | $(C_6H_5)_3Pb^-$ | ... | (8)[l] | ... | ... | ... |
| 64. | $Re(CO)_5^-$ | ... | (8)[l] | ... | ... | ... |
| 65. | $Mn(CO)_5^-$ | ... | (5.5)[l] | ... | ... | ... |
| 66. | $Co(CO)_4^-$ | ... | (3.5)[l] | ... | ... | ... |
| 67. | $HO_2^-$ | ... | (7.8)[m] | ... | ... | ... |

[a] J. O. Edwards, *J. Am. Chem. Soc.*, **76**, 1540 (1954); data in water. [b] "Handbook of Chemistry and Physics," 45th ed, Chemical Rubber Publishing Co., Cleveland, Ohio, 1964, pp D 76–78. [c] D. D. Perrin, Ed., "Dissociation Constants," Butterworth & Co., Ltd., London, 1965. [d] E. M. Arnett, *Progr. Phys. Org. Chem.*, **1**, 324 (1963). [e] M. M. Kreevoy, *et al.*, *J. Am. Chem. Soc.*, **82**, 4899 (1960). [f] K. Issleib and H. Bruchlos, *Z. Anorg. Allgem. Chem.*, **316**, 1 (1962). [g] C. A. Streuli, *Anal. Chem.*, **32**, 985 (1960); A. I. Bokanov, B. A. Korolev, and B. I. Stepanov, *Zh. Obshch. Khim.*, **34**, 1879 (1965), give 2.61 for $(C_6H_5)_3P$ and 8.86 for $(C_2H_5)_3P$. [h] Dissociation constant for $CH_3HgY \rightarrow CH_3Hg^+ + Y^-$: data at 20–25° from M. Schellenberg and G. Schwarzenbach, Proceedings of the 7th International Conference on Coordination Chemistry, Stockholm, 1962, p 158; *Helv. Chim. Acta*, **48**, 28 (1965); R. B. Simpson, *J. Am. Chem. Soc.*, **83**, 4711 (1961). Figures in parentheses are estimates based on formation constants of Ag(I); data in water. [i] T. R. Musgrave and R. N. Keller, *Inorg. Chem.*, **4**, 1793 (1965). [j] H. K. Hall, Jr., *J. Am. Chem. Soc.*, **79**, 5441 (1957). [k] Estimated from data in ref 6. [l] Estimated from relative data in diglyme reported by R. E. Dessy, R. L. Pohl, and R. B. King, *J. Am. Chem. Soc.*, **88**, 5121 (1966). [m] Estimated from rates of $OH^-$ and $O_2H^-$ with benzyl bromide: R. G. Pearson and D. N. Edgington, *ibid.*, **84**, 4607 (1962). [n] J. H. Beale, Ph.D. Thesis, Brown University, 1966. Values corrected to water. [o] 2,6-DMP = 2,6-dimethylpyridine; N,N-DHA = N,N-dimethylcyclohexylamine.

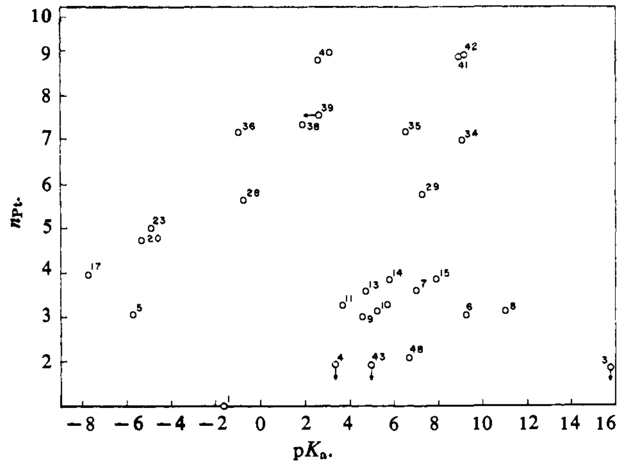

Figure 2. Plot of $n_{Pt}$ against p$K_a$. The numbers refer to the nucleophiles as listed in Table III.

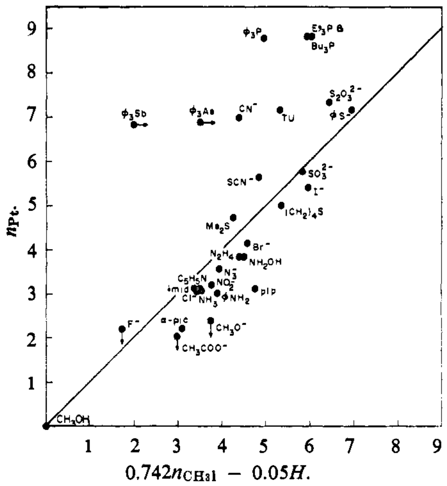

Figure 3. Plot of $n_{Pt}$ against right-hand side of eq 13. If the equation were obeyed, all points would be on the line.

earlier, in methanol the p$K_a$ values for the anionic bases would be increased by four units or so, and the p$K_a$ of the neutral bases would be little changed. A plot of $n_{CH_3I}$ against p$K_a$ looks about like Figure 2.

There are a number of indications that proton basicity has more effect on rates with methyl iodide than with the platinum complex, however. For example, methoxide ion, which is very basic, is a good nucleophile toward methyl iodide but a very poor reagent for *trans*-[Pt(py)$_2$Cl$_2$]. Triphenylphosphine, which is less basic than triethyl- and tributylphosphine, reacts more slowly with methyl iodide than do the other two phosphines, but its reaction rate with the platinum complex is almost identical with the rates of the two alkylphosphines. If the donor atom is held constant, the rate constant toward methyl iodide generally increases markedly with increasing base strength. This is not true for the platinum complex, as shown by the amines, for a second example. Thus proton basicity plays a smaller role in influencing reactivity toward platinum(II) than it does toward methyl iodide.

On the other hand, softness seems to be much more important for Pt, but it is difficult to find a suitable quantitative measure. One possible measure is $E_n$, the electrode potential of the oxidation

$$2Y_{aq}^- \rightleftharpoons Y_{2,aq} + 2e_{aq}^- \qquad (9)$$

normalized to $E_n = 0$ for Y = H$_2$O.

The Edwards equation

$$\log (k_Y/k_S) = \alpha E_n + \beta H \qquad (10)$$

has been quite successful in correlating a very wide range of data, including both kinetic and thermodynamic results from organic and inorganic systems.[5] Davis, in particular, has shown that eq 10 is quantitatively good for both nucleophilic displacements on tetrahedral carbon and divalent sulfur.[30] Since $H$ in eq 10 is p$K_a$ + 1.74, it is suggested that the equation be called the oxibase scale.[31]

A major disadvantage is that $E_n$ values are determinable for very few reagents. Of those shown in Table III, the ones in parentheses are calculated from rate data, assuming eq 10 to be valid. Sometimes misleading conclusions can be drawn from considering a limited amount of data. For example, there is a reasonably good correlation between the $E_n$ values of Table III and the $n_{CH_3I}$ values. Only cyanide ion and fluoride ion are badly off the line. Equation 10 becomes

$$n_{CH_3I} = 3.43E_n \qquad (11)$$

with $\beta$ equal to zero. In the same way there is a fairly good fit to the equation

$$n_{Pt} = 2.54E_n - 0.05H \qquad (12)$$

though methoxide ion is badly off, if the $E_n$ value of OH$^-$ is used.

It is obvious that if both (11) and (12) were valid, one could write

$$n_{Pt} = \left(\frac{2.54}{3.43}\right)n_{CH_3I} - 0.05H \qquad (13)$$

Figure 3 shows a plot of $n_{Pt}$ against the right-hand side of (13). All points should be on the line if the equation were obeyed. The nature of the deviations is such that the softer nucleophiles, such as the phosphines, are above the line and the harder nucleophiles, such as CH$_3$O$^-$ and CH$_3$COO$^-$, are below the line. No combination of $n_{Pt}$, $n_{CH_3I}$, and either $E_n$ or $H$ works much better than eq 13.

An attempt was also made to correlate the $n$ values with p$K_{CH_3Hg^+}$ or some combination of p$K_{CH_3Hg^+}$, $H$, or $E_n$. A very rough correlation does indeed exist between either of the $n$ values and p$K_{CH_3Hg^+}$. However, it is far from satisfactory, nor is it possible to greatly improve it by a consideration of $H$ or $E_n$ as well.

It is, of course, possible to use the $n_{Pt}$ values to predict the rates of reaction of other platinum complexes with various nucleophiles.[7] However, even in this restricted usage, substantial deviations can occur.[32] In the same way it is possible to use $n_{CH_3I}$, or the original $n_{CH_3Br}$ values (in water) of Swain and Scott,[6] to predict rates of nucleophilic displacements on several organic substrates. However, the range of usefulness is limited.[4] For example, reactions at carbonyl carbon in esters and acyl halides usually do not correlate

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(30) R. E. Davis, "Survey of Progress in Chemistry," A. Scott, Ed., Academic Press Inc., New York, N. Y., 1964; see also O. Foss, *Acta Chem. Scand.*, 4, 404, 866 (1950).

(31) R. E. Davis, *J. Am. Chem. Soc.*, 87, 3010 (1965).

(32) L. Cattalini, A. Orio, and M. Nicolini, *ibid.*, 88, 5734 (1966); U. Belluco, M. Graziani, and P. Rigo, *Inorg. Chem.*, 5, 1123 (1966).

well with $n_{CH_3Br}$ or $n_{CH_3I}$. This electrophilic center is harder, resembling the proton. As a result a Brønsted relationship is approximately obeyed.[33] If a restriction is made to a single donor atom, such as nitrogen, then the Swain–Scott correlation does extend over a wider range of substrates.[34] However, difficulties appear with either the Swain–Scott correlation, or the Brønsted relation, if several donor atoms are included.[35] The $\alpha$ effect, added reactivity due to the presence of an unshared pair of electrons on the atom $\alpha$ to the donor atom, is also a complicating feature. Thus some substrates show a large $\alpha$ effect; others show no $\alpha$ effect.[36] It is obvious that it would be difficult to include such behavior in any equation with either one or two parameters to describe the nucleophile. Steric factors are also not completely taken care of in the Edwards or Swain–Scott equations.

A plot of $n_{CH_3I}$ against $n_{CH_3Br}$ is linear, with some deviations. The equation is[37]

$$n_{CH_3I} = 1.4n_{CH_3Br} \tag{14}$$

Equation 14 shows an increasing relative reactivity toward methyl iodide of the more reactive, softer nucleophiles. This appears to be a consequence of the symbiotic effect.[37] A transition state containing a soft entering group and a soft leaving group has an extra stabilization. Since iodide ion is softer than bromide ion, the slope in eq 14 is greater than unity.

Such symbiosis between the entering and leaving group seems to be a general phenomenon in both organic and inorganic chemistry.[38] For example, the coefficient $\alpha$ in eq 10 increases steadily as the softness of the leaving group X in $CH_3X$ increases. There is a linear relationship between $\alpha$ and $E_n$ of the leaving group, which enables $\alpha$ values to be estimated *a priori* for certain cases.[31]

Our final conclusion is that at present it is not possible to predict quantitatively the rates of nucleophilic displacement reactions when a number of substrates of widely varying properties are considered. One can make reasonable estimates of what are apt to be good nucleophiles or poor nucleophiles. The present quantitative relationships for nucleophilic reactivity have limited ranges of application, though the Swain–Scott and Edwards equations can be quite useful.

**Acknowledgment.** This work was supported by the U. S. Atomic Energy Commission under Grant No. At(11-1)-1087.

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