peroxide (VI) in path a or to a four-membered one (VII) in path b.[11] Decarbonylation of VI to depside VIII in path a has an analogy.[12] In path b, keto acid IX which was derived from VII might be transformed into VIII by decarbonylation or by oxidative decarboxylation. In order to distinguish between the two modes of elimination of one carbon atom from keto acid IX, *p*-anisylglyoxylic acid was photooxidized in the presence of bengal rose. After irradiation with visible light, *p*-anisic acid (19%) and carbon dioxide (30%) were obtained, in addition to recovery (54%) of *p*-anisylglyoxylic acid, but no carbon monoxide could be detected.[13] These results suggest that the photosensitized oxygenation of 3-hydroxyflavones may proceed through path a simultaneously with path b. It seems reasonable to assume that the enzymatic cleavage of quercetin leading to depside IIa and carbon monoxide may proceed by a mechanism similar to path a.

Acknowledgment. The authors are grateful to Emeritus Professor M. Kotake and Professor T. Kubota for their encouragement throughout this work.

(11) Concerted cleavage processes in which a cyclic peroxide (VI or VII) is not involved may also be possible, instead of path a and path b.

(12) N. M. Bikales and E. I. Becker, *J. Org. Chem.*, 21, 1405 (1956).

(13) On irradiation with a high-pressure mercury lamp (Pyrex filter) in the presence and in the absence of sensitizer, *p*-anisylglyoxylic acid reacted with oxygen much faster to yield anisic acid and carbon dioxide. However, it was recovered unchanged when irradiated by visible light under oxygen without sensitizer.

Teruo Matsuura, Hideo Matsushima
Department of Synthetic Chemistry, Faculty of Engineering
Kyoto University, Kyoto, Japan

Harushige Sakamoto
Institute of Organic Chemistry, Faculty of Science
Osaka City University, Osaka, Japan

Received June 16, 1967

The Hydration Number and Rate of Water Exchange of the Trimethylplatinum(IV) Ion in Aqueous Solution Determined by Oxygen-17 Nuclear Magnetic Resonance[1]

Sir:

Recently we made a study of the hydration of organometallic ions in aqueous solution. Among the ions investigated was an unusual d^6 platinum(IV) complex whose properties are in marked contrast to those of other octahedral complexes of tetravalent platinum. Trimethylplatinum(IV) halides react with aqueous solutions of $AgNO_3$ or $AgClO_4$ to yield electrolyte solutions containing the trimethylplatinum(IV) cation. The pmr spectra of these solutions show a triplet (1:4:1) centered at τ 8.90 ppm. The similarity of the coupling constant $J_{^{195}Pt-CH_3}$ for the aquo ion to that of $[Pt(CH_3)_3(OH)]_4$ suggests that the aquo ion is probably *cis*-$[Pt(CH_3)_3(OH_2)_3]^+$.[2]

The ^{17}O nmr spectra of solutions of $(CH_3)_3PtClO_4$ indicate that the exchange of coordinated water molecules is *fast* at room temperature. The time scale of the ^{17}O resonance experiment was shortened by using $Dy(ClO_4)_3$ concentrations of up to 1.2 *m* to shift the bulk water signal as much as 3500–4000 cps upfield from the bound water resonance. At 5°, a signal for the water molecules bound in the first coordination sphere of the platinum(IV) is recorded clearly. As the sample is warmed to 29°, the bound-water signal disappears because of exchange. This is illustrated in Figure 1. By measuring the shift of the bulk water signal with respect to an external water standard for $Dy(ClO_4)_3$ solutions with and without $(CH_3)_3PtClO_4$, the hydration number of the trimethylplatinum(IV) ion has been found to be 3.0 ± 0.1 by the molal shift method.[3,4] The data are listed in Table I, and the hydration number, *n*, was calculated using the relation

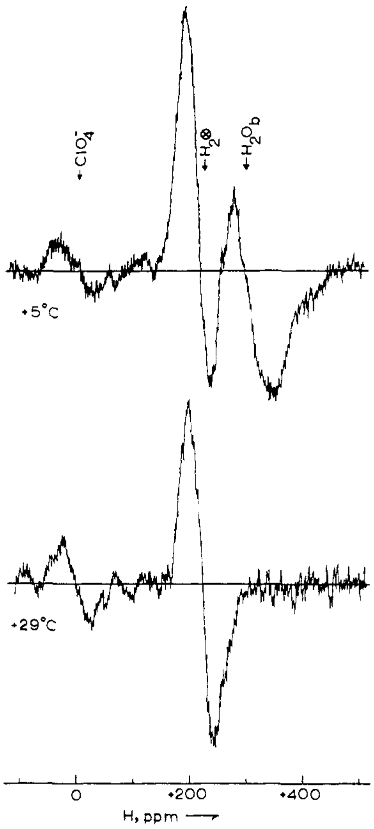


Figure 1. Oxygen-17 nmr spectra showing the bound-water resonance with respect to an external water sample. Solution composition: 1.969 *m* $(CH_3)_3PtClO_4$, 0.802 *m* $Dy(ClO_4)_3$, 0.486 *m* $HClO_4$.

$$n = \frac{55.5}{[(CH_3)_3Pt^{IV}]}\left[1 - \frac{(\delta_{H_2O}/[Dy^{+3}])_{ref}}{(\delta_{H_2O}/[Dy^{+3}])_{sample}}\right]$$

The bulk-water signal in these solutions is broadened considerably because of the exchange process. While the ^{17}O water resonance of a pure $Dy(ClO_4)_3$ solution sharpens as the temperature is raised from 5 to 29°, the signal for a solution containing $[Pt(CH_3)_3(OH_2)_3]^+$ broadens (see Figure 2). Using the relation for slow exchange together with the line-width measurements and considering the $Dy(ClO_4)_3$ solution as the solvent, the mean half-life of the water-exchange process has been estimated to be 1.4×10^{-3} sec at 5°.[5]

The very high rate of exchange of the coordinated water ligands in this complex compared with other octa-

---

(1) Research sponsored by AFOSR (SRC)-OAR, USAF Grant No. AF-AFOSR-691-65 and -67.

(2) K. Kite, J. A. S. Smith, and E. J. Wilkins, *J. Chem. Soc., Sect. A*, 1744 (1966).

(3) M. Alei and J. A. Jackson, *J. Chem. Phys.*, 41, 3402 (1964).

(4) J. A. Jackson, J. F. Lemons, and H. Taube, *ibid.*, 32, 553 (1960).

(5) The experimental details of the oxygen-17 resonance measurements and the kinetic studies will be published elsewhere.

Table I. Primary Hydration Number of Trimethylplatinum(IV)[a]

$[(CH_3)_3Pt^+]$, *m*	$[Dy^{+3}]$, *m*	$[H^+]$, *m*	δ_{H_2O},[b] ppm	$\delta_{H_2O}{}^b/[Dy^{+3}]$, ppm m^{-1}	δ_{H_2O},[c] ppm	$\delta_{H_2O}{}^c/[Dy^{+3}]$, ppm m^{-1}
2.167	0.434	0.520	212 ± 2	488		
1.969	0.802	0.486	397 ± 2	495	449 ± 1	560
1.758	1.197	0.451	585 ± 2	489	661 ± 2	552
0	0.406	0.051	188 ± 2	463		
0	0.829	0.033	380 ± 2	458	413 ± 1	498
0	1.194	0.043	547 ± 2	458	599 ± 1	502

[a] Resonance measured at 7.66 Mc/sec; solutions enriched to 4.5 atom % ^{17}O. [b] At 29°. [c] At 5°.

hedral platinum(IV) and d^6 complexes, in general,[6] illustrates the labilizing effect on the other ligands caused by alkyl groups in the first coordination sphere. This has been recognized previously for platinum(II) complexes.[7] It seems likely that the coordinated water molecule in aquocobalamin (vitamin B_{12a}) which is *trans* to a carbanion ligand in this d^6 cobalt complex has at least as high an exchange rate, and this is in agreement with the observation that substitution reactions proceed rapidly at this site.[8–10]

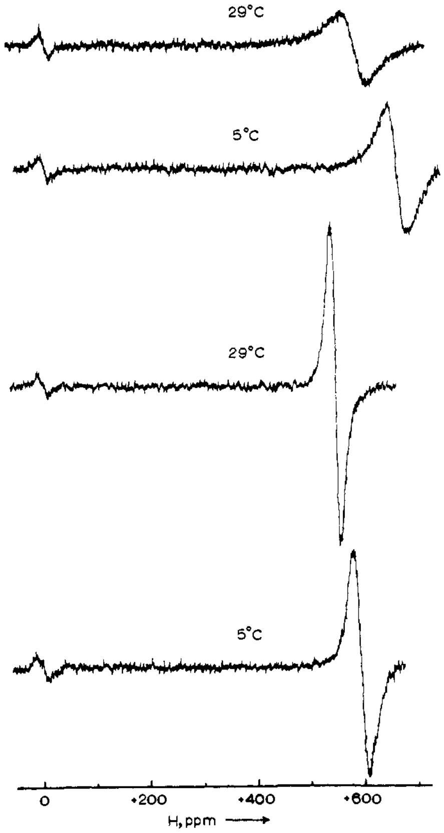


Figure 2. Bulk-water resonance with respect to an external water sample. Solution composition: (top spectra) 1.758 *m* $(CH_3)_3PtClO_4$, 1.197 *m* $Dy(ClO_4)_3$, 0.451 *m* $HClO_4$; (bottom spectra) 1.194 *m* $Dy(ClO_4)_3$, 0.043 *m* $HClO_4$.

Since the suggestion by Jackson, Lemons, and Taube that oxygen-17 nmr might be used to count the number of water molecules in the first coordination sphere of metal ions,[4] hydration numbers have been determined only for Be^{+2} (4.2 ± 0.1,[11] 3.8 ± 0.1[3]), Al^{+3} (5.9 ± 0.1[3,11]), and Ga^{+3} (6.28 ± 0.26, 5.89 ± 0.20;[12] 5.9 ± 0.1[13]).

---

[6] For example, the half-life for exchange of $Rh(OH_2)_6{}^{+3}$ is *ca.* 33 hr at 64.4°: W. Plumb and G. Harris, *Inorg. Chem.*, **3**, 542 (1964).

[7] F. Basolo and R. G. Pearson, *Progr. Inorg. Chem.*, **4**, 381 (1962).

[8] R. A. Firth, H. A. O. Hill, J. M. Pratt, R. G. Thorp, and R. J. P. Williams, *Chem. Commun.*, 400 (1967).

[9] J. M. Pratt and R. G. Thorp, *J. Chem. Soc., Sect. A*, 187 (1966).

[10] G. C. Hayward, H. A. O. Hill, J. M. Pratt, N. J. Vanston, and R. J. P. Williams, *J. Chem. Soc.*, 6485 (1965).

[11] R. E. Connick and D. N. Fiat, *J. Chem. Phys.*, **39**, 1749 (1963).

[12] D. Fiat and R. E. Connick, *J. Am. Chem. Soc.*, **88**, 4754 (1966).

[13] T. J. Swift, O. G. Fritz, Jr., and T. A. Stephenson, *ibid.*, **46**, 40 (1967).

[14] NASA Trainee, 1964–1967.

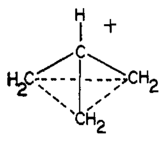
Gary E. Glass,[14] R. Stuart Tobias
Department of Chemistry, University of Minnesota
Minneapolis, Minnesota 55455

Received August 24, 1967

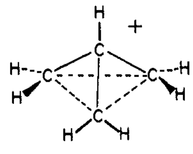
Stability and Symmetry of the 8,9-Dehydro-2-adamantyl Cation

Sir:

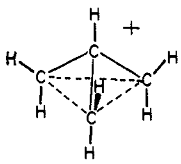
A nonclassical tricyclobutonium ion intermediate with C_{3v} symmetry (**1**) was initially proposed[1,2] to rationalize the unexpectedly high reactivity of cyclopropylcarbinyl halides[3] and benzenesulfonate[2] and the remarkable degree of equivalence achieved by the three methylene groups during the nitrous acid deamination of cyclopropylcarbinylamine-α-C^{14}.[1] It has subsequently gained disfavor as an intermediate, but retained prominence as a possible transition-state species connecting other less symmetrical ions.[4,5] Of the two geometries for a tricyclobutonium ion, **2** and **3**, the former has seemed favored by molecular orbital calculations[6] and the latter by geometrical considerations.[4]



1



2



3

We now report that the solvolysis of 8,9-dehydro-2-adamantyl 3,5-dinitrobenzoate (**4**), a system potentially capable of generating a carbonium ion of C_{3v} symmetry geometrically analogous to **3** but unable to adopt a form similar to the alternative conformation **2**, occurs with the marked rate acceleration characteristic of cyclopro-

---

[1] J. D. Roberts and R. H. Mazur, *J. Am. Chem. Soc.*, **73**, 3542 (1951).

[2] C. G. Bergstrom and S. Siegel, *ibid.*, **74**, 145 (1952).

[3] J. D. Roberts and R. H. Mazur, *ibid.*, **73**, 2509 (1951).

[4] R. H. Mazur, W. N. White, D. A. Semenow, C. C. Lee, M. S. Silver, and J. D. Roberts, *ibid.*, **81**, 4390 (1959).

[5] P. von R. Schleyer and G. W. Van Dine, *ibid.*, **88**, 2321 (1966), and references therein.

[6] M. E. H. Howden and J. D. Roberts, *Tetrahedron Suppl.*, **2**, 403 (1963).