Journal of Organometallic Chemistry, 56 (1973) 103–109

DETERMINATION OF THE STEREOCHEMISTRY OF ETHYLENE METHOXYMERCURATION BY NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY

TAKASHI IBUSUKI and YASUKAZU SAITO
Department of Synthetic Chemistry, Faculty of Engineering, University of Tokyo, Bunkyoku, Tokyo (Japan)
(Received November 24th, 1972)

SUMMARY

The complete stereospecificity of ethylene methoxymercuration has been confirmed using NMR spectroscopy by comparing methoxymercurated *trans*-ethylene-1,2-d_2 with methoxymercurated *cis*-ethylene-1,2-d_2. On the basis of the solvent effects on the vicinal proton–proton coupling constants of these compounds, we have identified the former as *erythro*-1,2-*dideuterio*-2-methoxyethylmercuric chloride and the latter as the *threo* isomer. The stereochemistry of ethylene methoxymercuration is thus concluded to be an exclusively *anti* addition.

INTRODUCTION

Considerable stereochemical interest has been evoked in the oxymercuration of olefins[1–4]. Among cyclic olefins, exclusive *syn* addition for *trans*-cyclooctene[5] and norbornene[6] has attracted special attention. The stereospecificity of the former is ascribed to the steric hindrance of the methylene chain, since the oxygen-containing parts of the molecules are prevented from back side attack on the double bond of the mercurinium ion intermediate[5]. The latter case is interpreted as a result of reduced internal strain in the transition state[2]. Similar arguments have been invoked for bicyclo[2.1.1]hexene[7] and for the addition of mercuric azide to cyclopropene[8].

In contrast, the stereochemistry for bicyclo[2.2.2]octene is dependent not only on the concentration and the nature of the oxy anion but also on the polarity of the solvent[9–11]. Although the *syn* process has been proposed to be due to either a four-centered or a six-centered transition state by Traylor[2,10], a common intermediate for *syn* and *anti* addition, *i.e.*, a solvated mercurinium ion, was suggested by Bach[11], in which *syn* addition occurs when the ion-pair disintegrates at the front side of double bond. Such an interpretation is interesting from the viewpoint of complex catalysis[12], since the stereochemistry is determined by ligand effects on the mercury. Ligand insertion also plays an important role[13] in olefin oxypalladation during the Wacker reaction[14].

Oxymercuration of cyclic olefins usually results in *anti* stereochemistry[1]. Recently, oxymercuration of acenaphthylene[15] and indene[16] were shown to occur in the *anti* manner in spite of the *syn* predominance in hydrohalogenation[17]. The stereochemistry of oxymercuration has previously been determined by the use of kinetics[18], X-ray diffraction[19], and IR[6], or NMR spectroscopy[11,20–22].

With acyclic olefins, however, conformational analysis applied to freely rotating oxymercurials cannot afford the mode of addition. Thus the methoxy and iodomercury groups of 2-methoxyethylmercuric iodide were ascertained by IR spectroscopy to be in *trans* positions in the solid state[23], but an *anti* addition to ethylene was not deduced[3]. The stereospecificity of the oxymercuration–deoxymercuration of the 2-butenes is apparent, since both of the starting 2-butenes are exclusively regenerated[24]. The stereochemistry was determined from the relative magnitude of the deoxymercuration of *anti* and *syn* adducts of methoxymercurated cyclohexene, where the former is approximately 10^6 times faster than the latter[18]. The observed rates of regeneration of *trans*- and *cis*-2-butene were reported to be 13.8 ± 0.81 and 13.6 ± 0.71 $\mathrm{mol^{-1} \cdot sec^{-1}}$, together with activation energies of 15.2 ± 0.7 and 14.8 ± 0.3 $\mathrm{kcal \cdot mol^{-1}}$, respectively[24]. The lack of unequivocal evidence for *anti* addition with simple olefins was pointed out by Fahey[4], who proposed an *AdE*3 *anti* addition mechanism for oxymercuration.

In the present work we report the oxymercuration of the simplest olefin, ethylene, stereospecifically deuterated at the *trans* and *cis* positions. The stereochemistry of its oxymercuration and the configurational identification of the products can be determined by the solvent effects on the vicinal proton–proton coupling constants of 1,2-*dideuterio*-2-methoxyethylmercuric chlorides.

EXPERIMENTAL

Both *trans*-ethylene-1,2-d_2 and *cis*-ethylene-1,2-d_2 were prepared by the method of Nicholas[25]. These deuterated ethylenes were identified by infrared spectroscopy using a JASCO IRA-2 spectrometer in the rocksalt region. Isotropic and isomeric purities were confirmed by the fact that an intense absorption band at 987 $\mathrm{cm^{-1}}$ was observed for gaseous *trans*-ethylene-1,2-d_2 without any band around 842 $\mathrm{cm^{-1}}$ at 90 mmHg, and *vice versa* for *cis*-ethylene-1,2-d_2[26].

2-Methoxyethylmercuric chloride and the 1,2-*dideuterio*-2-methoxyethylmercuric chlorides were prepared according to the usual method[27]. The solutions (20 wt%) of these mercurials in various solvents were analyzed at 24° by JEOL PS-100 (100 MHz) and Hitachi R-20 B (60 MHz) NMR spectrometers. Deuterium decoupling was carried out for the deuterated mercurials with JEOL JNM-OA-1 or Takeda–Riken 3130 synthesizers. The chemicals used here were obtained from standard commercial sources and were used without further purification.

RESULTS

1. *Stereospecificity in methoxymercuration toward ethylene*-1,2-d_2

An NMR spectrum of methoxymercurated *trans*-ethylene-1,2-d_2 (I) dissolved in dimethyl sulfoxide is shown in Fig. 1(a). The doublets of an AB spin system, appearing at δ 1.850 and 3.560 ppm from internal TMS standard, were assigned to the methylene protons with the carbons substituted by the chloromercury and methoxy groups, respectively[28]. The vicinal proton–proton coupling constant was determined to be 9.31 Hz from the splitting of the doublets. The four small sets of doublet peaks were interpreted as the satellites due to the vicinal and geminal proton–mercury (^{199}Hg; $I = 1/2$, natural abundance 16.84%) spin–spin interactions. A similar spectrum was obtained for methoxy-mercurated *cis*-ethylene-1,2-d_2 (II), for which chemical shifts of 1.852 and 3.559 ppm and a coupling constant of 5.72 Hz were observed. The NMR spectrum of a 1/1 mixture of compounds (I) and (II) is also shown in Fig. 1 (b). The peaks of both (I) and (II) were observed to be separated owing to the large difference in the vicinal coupling constants for (I) and (II). It was also confirmed that

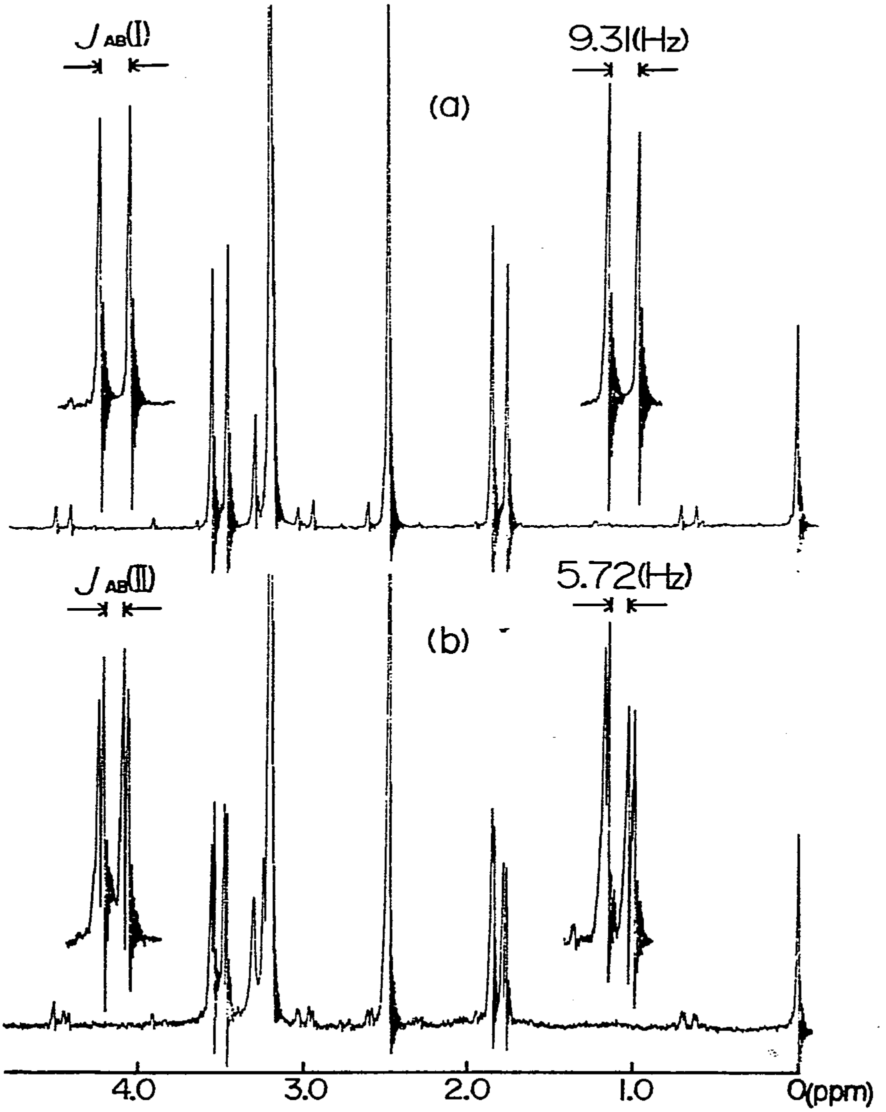

Fig. 1. (a) The NMR spectrum of methoxymercurated *trans*-ethylene-1,2-d_2(I). (b) The NMR spectrum of a 1/1 mixture of (I) and methoxymercurated *cis*-ethylene-1,2-d_2(II). These spectra were taken at 100 MHz in 20 wt% solution of dimethyl sulfoxide at 24° with internal TMS reference.

there was no superposition of NMR peaks for (II). The complete stereospecificity of the methoxymercuration of ethylene is thus established.

2. *Solvent effects on the vicinal proton–proton coupling constants of* 1,2-*dideuterio-2-methoxyethylmercuric chlorides*

The vicinal proton–proton coupling constants, J_{AB}, obtained in various solvents, are summarized in Table 1.

TABLE 1

VICINAL H–H COUPLING CONSTANTS OF METHOXYMERCURATED *trans*-ETHYLENE-1,2-d_2(I) AND *cis*-ETHYLENE-1,2-d_2(II), AND RELATED VALUES IN VARIOUS SOLVENTS[a]

Solvent	*J(I)* *(Hz)*	*J(II)* *(Hz)*	$J_{av}(1)$[b] *(Hz)*	$J_{av}(2)$[c] *(Hz)*
Chloroform	7.15	6.80	6.92	7.03
Dichloromethane	7.13	6.78	6.90	7.01
Acetone-d_6	7.92	6.40	6.91	7.41
Acetonitrile-d_3	8.22	6.25	6.91	7.56
Dimethyl sulfoxide	9.31	5.72	6.92	8.11

[a] All values are measured at 24° in 20 wt% solutions. [b] $J_{av}(1)$ means $(\frac{1}{3})[J(I)+2J(II)]$. See text. [c] $J_{av}(2)$ means $(\frac{1}{3})[2J(I)+J(II)]$. See text.

There are apparently opposing tendencies in the solvent dependence of J_{AB} for methoxymercurated *trans*-ethylene-1,2-d_2(I) and for methoxymercurated *cis*-ethylene-1,2-d_2(II). The former, J(I), increased with the polarity of solvents from 7.15 Hz in chloroform to 9.31 Hz in dimethyl sulfoxide, whereas the latter, J(II), decreased from 6.80 Hz in chloroform to 5.72 Hz in dimethyl sulfoxide. It is further to be noted that the values of J(I) were larger than those of J(II) in all the solvents investigated and that the more polar the solvent, the larger the magnitude of $J(I)-J(II)$.

DISCUSSION

1. *The stereochemistry of ethylene methoxymercuration as deduced from configurational identification of* 1,2-*dideuterio-2-methoxyethylmercuric chlorides*

Since the complete stereospecificity of methoxymercuration toward *trans*-ethylene-1,2-d_2 and *cis*-ethylene-1,2-d_2 is confirmed, these products must be diastereoisomers. The following two cases are therefore possible in connection with the mode of addition. The one case is an *anti* addition, where *trans*-ethylene-1,2-d_2 and *cis*-ethylene-1,2-d_2 afford *erythro*-1,2-*dideuterio*-2-methoxyethylmercuric chloride and the *threo* isomer, respectively. The other case is a *syn* addition, *i.e.*, the assignment of the diastereoisomers is opposite.

On the basis of the solvent and substituent effects on the vicinal proton–proton coupling constants of 2-methoxyethylmercuric chloride, we have identified the methoxymercurated *trans*-ethylene-1,2-d_2(I) as *erythro*-1,2-*dideuterio*-2-methoxyethylmercuric chloride and the methoxymercurated *cis*-ethylene-1,2-d_2(II) as the *threo* isomer in the following manner.

A. 2-Methoxyethylmercuric chloride is composed of two kinds of rotational isomers, the one with the chloromercury and methoxy groups disposed *trans*, and the other, two energetically equivalent enantiomers with two groups disposed *gauche*. n_t and $n_g = 1 - n_t$ are defined as the populations of the two kinds of rotamers, respectively. The vicinal proton–proton coupling constants of the *erythro* isomer (the methoxymercurated *trans*-ethylene-1,2-d_2), J(I), and that of the *threo* isomer (the methoxymercurated *cis*-ethylene-1,2-d_2), J(II), can be described as a function of the populations as follows[29]:

$$J(\mathrm{I}) = J_g + n_t(J_t - J_g) \tag{1}$$

$$J(\mathrm{II}) = (\tfrac{1}{2})[(J_t + J_g) - n_t(J_t - J_g)] \tag{2}$$

J_t and J_g are the vicinal coupling constants for the two protons disposed *trans* and *gauche*, respectively. Equation (3) is derived from eqns. (1) and (2).

$$J(\mathrm{I}) + 2\,J(\mathrm{II}) = J_t + 2\,J_g \tag{3}$$

The values of $(J_t + 2J_g)$ should be solvent independent, since both J_t and J_g should not be changed by solvents. It is widely recognized that the vicinal proton–proton coupling constants of rigid molecules which cannot undergo conformational changes, are solvent independent[30,31]. Some examples, those of styrene oxide[32], styrene sulfide[32], and 1,2,3,4,5,7,7-heptachloro[2.2.1]heptene[33,34], are shown in Fig. 2 as a function of the dielectric constants of the solvent. It is apparent that the lines are straight and parallel to the abscissa.

Thus the values of $J(\mathrm{I}) + 2J(\mathrm{II})$ in various solvents should be constant by considering eqn. (3) and Fig. 2. The average vicinal proton–proton coupling constants of 2-methoxyethylmercuric chloride, $J_{\mathrm{av}}(1) = (\frac{1}{3})[J(\mathrm{I}) + 2J(\mathrm{II})]$, are listed in Table 1 and added to Fig. 2. It is apparent that the plots of $J_{\mathrm{av}}(1)$ are parallel to the abscissa as expected.

B. On the assumption of the opposite assignment that the methoxymercurated *trans*-ethylene-1,2-d_2 is the *threo* isomer and the methoxymercurated *cis*-ethylene-1,2-d_2 is the *erythro* isomer, the average vicinal proton–proton coupling constants are described as $J_{\mathrm{av}}(2) = (\frac{1}{3})[2J(\mathrm{I}) + J(\mathrm{II})]$. The calculated values of $J_{\mathrm{av}}(2)$ in various solvents are listed in Table 1 and the plots are shown as the broken line in Fig. 2. This line is dependent on the dielectric constant of the solvent to a remarkable extent, which is anomalous in comparison with the lines of the examples given in Fig. 2. Thus the assignment deduced from the assumption of a *syn* addition has been disproved.

C. Finally, the magnitude of $J_{\mathrm{av}}(1)$ is very reasonable from the viewpoint of the substituent electronegativities, which have been ascertained for various 1,2-disubstituted ethanes by Abraham[35]. The average vicinal proton–proton coupling constant of 2-methoxyethylmercuric chloride, $J_{\mathrm{av}}^{\mathrm{calc}}$, is determined according to the equation:

$$J_{\mathrm{av}}^{\mathrm{calc}} = 18.0 - 0.8\Sigma E_i$$

The electronegativities of H, OCH_3, and HgCl substituents are taken as 2.1, 3.5, and 1.9, respectively[36]. The value of $J_{\mathrm{av}}^{\mathrm{calc}}$ is given as a broad line in Fig. 2. The coincidence of the broad line and the plots of $J_{\mathrm{av}}(1)$ strongly supports the validity of our assignment.

Thus the stereochemistry of methoxymercuration of the simplest olefin, ethylene, is definitely established as an exclusive *anti* addition.

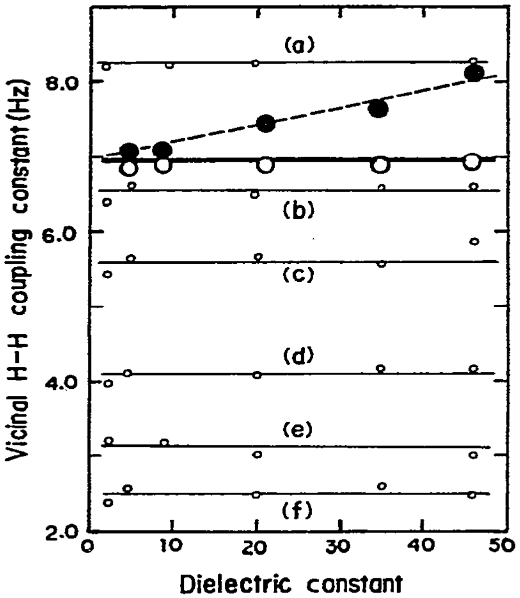

Fig. 2. Dependence of calculated vicinal proton–proton coupling constants for 1,2-*dideuterio*-2- methoxy-ethylmercuric chlorides and observed values for some rigid molecules on the dielectric constants of solvents. ○: Vicinal coupling constants calculated from the equation, $J_{av}(1) = (\frac{1}{3})[J(\text{I}) + 2J(\text{II})]$, for 1,2-*dideuterio*-
Fig. 2. Dependence of calculated vicinal proton–proton coupling constants for 1,2-*dideuterio*-2-methoxy-2-methoxyethylmercuric chlorides. See text. ●: Vicinal coupling constants calculated from the equation, $J_{av}(2) = (\frac{1}{3})[2J(\text{I}) + J(\text{II})]$, for the same compounds. See text. (a) J_{cis} of 1,2,3,4,5,7,7-heptachlorobicyclo-[2.2.1]heptene; (b) J_{cis} of the episulfide protons in styrene sulfide; (c) J_{trans} of the episulfide protons in styrene sulfide; (d) J_{cis} of the epoxy protons in styrene oxide; (e) J_{trans} of 1,2,3,4,5,7,7-heptachlorobicyclo-[2.2.1]heptene; (f) J_{trans} of the epoxy protons in styrene oxide.

2. *The preferred conformation of* 2-*methoxyethylmercuric chloride*

The preferred conformation of 2-methoxyethylmercuric chloride may be determined from the following equation, which is derived from eqns. (1) and (2)[29]:

$$J(\text{I}) - J(\text{II}) = (\tfrac{3}{2})(J_t - J_g)(n_t - \tfrac{1}{3}) \qquad (4)$$

It is generally accepted for substituted acyclic alkanes that J_t is always larger than J_g in accordance with the Karplus equation[37]. Thus the sign of $J(\text{I}) - J(\text{II})$ can reflect the preferred conformation of the compound.

As pointed out previously, $J(\text{I})$ is larger than $J(\text{II})$ in all the solvents investigated. It is therefore concluded that n_t is always larger than $\frac{1}{3}$, the equivalent population, and that the conformation with the chloromercury and methoxy groups disposed *trans* is more stable than the *gauche* conformation in all the solvents. This preference is emphasized in polar solvents, as can be seen from the fact that $J(\text{I}) - J(\text{II})$ is 3.59 Hz in dimethyl sulfoxide which is much larger than that of 0.35 Hz in chloroform.

ACKNOWLEDGEMENTS

The authors wish to express their gratitude to Prof. Yukio Yoneda for helpful discussion and encouragement. Financial support from the Kawakami Memorial Fund is acknowledged.

REFERENCES

1 W. Kitching, *Organometal. Chem. Rev.*, 3 (1968) 61.
2 T. G. Traylor, *Accounts Chem. Res.*, 2 (1969) 152.
3 N. S. Zefirov, *Russ. Chem. Rev.*, 34 (1965) 527.
4 R. C. Fahey, *Top. Stereochem.*, 3 (1968) 237.
5 (a) V. I. Sokolov, L. L. Troitskaya and O. A. Reutov, *Dokl. Akad. Nauk, SSSR*, 166 (1966) 136;
(b) V. I. Sokolov, L. L. Troitskaya and O. A. Reutov, *J. Organometal. Chem.*, 17 (1969) 323.
6 (a) T. G. Traylor and A. W. Baker, *Tetrahedron Lett.*, (1969) 14;
(b) T. G. Traylor and A. W. Baker, *J. Amer. Chem. Soc.*, 85 (1963) 2746.
7 F. T. Bond, *J. Amer. Chem. Soc.*, 90 (1968) 5326
8 J. E. Galle and A. Hassner, *J. Amer. Chem. Soc.*, 94 (1972) 3930.
9 T. G. Traylor, *J. Amer. Chem. Soc.*, 86 (1964) 244.
10 T. T. Tidwell and T. G. Traylor, *J. Org. Chem.*, 33 (1968) 2614.
11 R. D. Bach and R. F. Richter, *J. Amer. Chem. Soc.*, 94 (1972) 4747.
12 Y. Saito, *J. Electrochem. Soc. Japan*, 40 (1972) 175.
13 R. S. Nyholm, *Proc. Third Congr. Cat., Amsterdam*, (1964) 25.
14 P. M. Henry, *J. Amer. Chem. Soc.*, 86 (1964) 2246.
15 V. I. Sokolov, L. L. Troitskaya and O. A. Reutov, *Zh. Org. Khim.*, 5 (1969) 174.
16 A. Toyoda and Y. Saito, Submitted for publication.
17 (a) M. J. S. Dewar and R. C. Fahey, *J. Amer. Chem. Soc.*, 85 (1963) 2245;
(b) M. J. S. Dewar and R. C. Fahey, *J. Amer. Chem. Soc.*, 85 (1963) 2248.
18 M. M. Kreevoy and F. R. Kowitt, *J. Amer. Chem. Soc.*, 82 (1960) 739.
19 A. G. Brook and G. F. Wright, *Acta Crystallogr.*, 4 (1951) 50.
20 (a) M. M. Anderson and P. M. Henry, *Chem. Ind. (London)*, (1961) 2053;
(b) S. Wolfe and P. G. Campbell, *Can. J. Chem.*, 43 (1965) 1184.
21 W. L. Waters, *Tetrahedron Lett.*, (1969) 3769.
22 R. F. Richter, J. C. Phillips and R. D. Bach, *Tetrahedron Lett.*, (1972) 4327.
23 M. M. Kreevoy and L. T. Ditsch, *J. Amer. Chem. Soc.*, 82 (1960) 6124.
24 M. M. Kreevoy, L. L. Schaleger and J. C. Ware, *Trans. Faraday Soc.*, 58 (1962) 2433.
25 P. P. Nicholas and R. T. Carroll, *J. Org. Chem.*, 33 (1969) 2345.
26 R. L. Arnet and B. L. Crawford, Jr., *J. Chem. Phys.*, 18 (1950) 118.
27 K. Ichikawa, H. Ouchi and S. Arai, *J. Amer. Chem. Soc.*, 82 (1960) 3880.
28 F. A. Cotton and J. R. Leto, *J. Amer. Chem. Soc.*, 80 (1958) 4823.
29 L. M. Jackmann and S. Sternhell, *Application of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry*, 2nd Ed., Pergamon, New York, 1969, p. 291.
30 P. Laszro, *Progr. NMR Spectr.*, 3 (1967) 231.
31 R. J. Abraham, *J. Phys. Chem.*, 73 (1969) 1192.
32 S. L. Smith and R. H. Cox, *J. Chem. Phys.*, 45 (1966) 2848.
33 S. L. Smith and R. H. Cox, *J. Phys. Chem.*, 72 (1968) 198.
34 R. H. Cox and L. W. Harrison, *J. Magn. Resonance*, 6 (1972) 84.
35 R. J. Abraham, *Mol. Phys.*, 7 (1963) 165.
36 H. O. Pritchard and H. A. Skinner, *Chem. Rev.*, 55 (1955) 745.
37 M. Karplus, *J. Amer. Chem. Soc.*, 85 (1963) 2870.