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CHEMICAL IONIZATION MASS SPECTROMETRY OF ARENE-CHROMIUM AND -MOLYBDENUM COMPLEXES

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Summary

The CH_4 CI mass spectra of arenechromium tricarbonyls (Ar = benzene, toluene, fluorobenzene, chlorobenzene, mesitylene, and methyl benzoate), mesitylenemolybdenum tricarbonyl, cycloheptatrienechromium tricarbonyl, and dibenzenechromium have been obtained. The spectra are interpreted in terms of predominant metal protonation of the complexes. The most abundant ion in the spectrum of dibenzenechromium is the molecular ion which perhaps results from H atom loss from the protonated ion. Comparisons are made between gaseous ionic and solution behavior of these compounds.

Introduction

Recently, the chemical ionization (CI) mass spectra of several organometallic compounds have been reported [1]. Those spectra are generally simple and appear to be useful for characterization of organometallic compounds. We report a similar study on the methane CI spectra of some organometallic derivatives of Cr. These spectra are quite simple, can be used readily for characterization, show strong similarities to each other, and reflect some of the known chemistry of these compounds in the condensed phase.

The technique of chemical ionization mass spectrometry has been adequately reviewed elsewhere [2, 3]. Continuing previous practice, we used methane as the CI reagent gas; consequently, the major reactant ions which produce the ionization of the organometallic compound are CH_5^+ and $C_2H_5^+$. These ions are expected to react mostly by H^+ and H^- transfer, perhaps with subsequent dissociation [2, 3].

The compounds with which we shall be concerned are the following: $ArCr(CO)_3$, Ar = benzene, toluene, mesitylene, chlorobenzene, fluorobenzene

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and methyl benzoate; mesitylenemolybdenum tricarbonyl; cycloheptatriene-chromium tricarbonyl; and dibenzenechromium.

Experimental

The carbonyl compounds were prepared by thermal reactions of the arene with $Cr(CO)_6$ or $Mo(CO)_6$ by modifications of methods previously reported [4]. Tetrahydrofuran was used instead of diethylene glycol dimethyl ether in a 1/1 by volume mixture with the hydrocarbon. Loss of the hexacarbonyl was prevented during reflux by a technique discussed elsewhere [5]. Dibenzenechromium was purchased from Alfa Inorganics.

Carbon and hydrogen analyses were performed by Microanalyses, Wilmington, Delaware, and were within ± 0.5% of the theoretical values. The products were characterized by comparison of carbonyl stretching frequencies with published values [6—8].

Because of the air sensitivity of the compounds, all purifications were done in a nitrogen-filled dry box and the samples used for mass spectral analyses were kept under nitrogen or in a vacuum desiccator until shortly before use. For the most sensitive compounds, capillaries were filled and sealed with stopcock grease within the dry box. Immediately before sample introduction, a short section of the capillary was sealed with a small flame and the tip of the capillary was broken within the vacuum system. Volatile impurities were detected in some samples which were removed by fractional sublimation within the vacuum system.

The spectra were obtained with a CEC (duPont) 21-110B mass spectrometer which has been modified for high pressure operation [9, 10]. The samples were introduced with a direct insertion probe at source temperatures from 50—125°, depending on the compound. The temperature of the sample is not accurately known and is somewhat lower than the source temperature.

The spectra were obtained at methane pressures of 0.6 to 1.0 mm, but no systematic pressure variation was observed. The methane was passed through a glass coil immersed in liquid nitrogen to remove water, and the 19/17 ratio, H_3O^+/CH_5^+, was generally < 0.1. The repellers were set at 3—5 V, corresponding to a maximum ion energy of 2—3 V and a field strength of 7—12 V/cm. The energy of the electrons was 430—570 V.

The spectra reported in this paper are averages of at least three determinations. The average deviation of the abundances of the major ions is less than ± 10%. The data are reported as percentages of the sample ionization, $10^2 I_i/\Sigma I_i$ rather than as percentages of the most abundant peak. ΣI_i represents the sum of peak heights (= ion currents) for all masses which were not present in the spectrum of 'pure methane'. The abundances of some minor ions in the spectrum of methane depend on the purity of the gas and the cleanliness of the mass spectrometer and inlet system.

It is worthwhile noting some of the difficulties associated with obtaining reproducible and meaningful CI spectra of these compounds. Some of these observations may be useful in explaining variations in the electron ionization (EI) spectra. The EI spectra of cycloheptatriene—$Cr(CO)_3$ have been reported [11—13] and in these spectra the ratio of cycloheptatriene ions (*m/e* 91 and 92) to the most abundant chromium-containing ion, Cr^+, ranges from 2 to 0.1, depending upon the experimental conditions. For benzenechromium tricarbonyl, the spectra obtained over a wide range of conditions showed that the fractional abundance ($= I_i/\Sigma I_i$) of protonated benzene (*m/e* 79) varied from 0.25 to 0.02: $C_6H_7^+$ was under some conditions the most abundant ion in the spectrum and under others, a minor component. The sample of $C_6H_6Cr(CO)_3$ was introduced with a direct insertion probe at source temperatures of 60—95° and over this range the fractional abundances of $C_6H_7^+$ decreased with increasing temperature. If the sample was allowed to remain in the source for a substantial period of time at a nominally constant temperature, the fractional abundance of $C_6H_7^+$ decreased with increasing time. We attribute this behavior (which was observed for all of the compounds in this study) to the presence of a small amount of free arene present in the sample when it was introduced into the mass spectrometer since the hydrocarbons are substantially more volatile than the organometallic compounds. These trace amounts of arenes could be residual amounts remaining after synthesis, or they could be produced by air oxidation of the arenechromium tricarbonyls during the time of sample preparation and introduction. In addition, if one heats the samples too much, then decomposition begins to occur, as evidenced by an increase in fractional abundance of characteristic ligand ions with increasing temperature.

The data reported here, therefore, represent the spectra obtained under conditions found to give the minimum values for abundances of characteristic ligand ions and the amounts reported represent the maximum values of aromatic ions which could be formed from fragmentation of the organometallic ions. It is likely that the small amounts of arene ions which we see, result from ionization of small amounts of molecular decomposition products and not from fragmentation of protonated molecular ions.

It is not possible to measure directly the pressures of samples introduced into the source of a mass spectrometer with a direct insertion probe. In both CI and EI mass spectra, ions have been observed at masses higher than the molecular weights of the compounds under analysis which have been attributed to neutral dimers or gaseous ion-molecule reactions [1, 11, 14—17].

Reactions of organometallic ions of these compounds with the organometallic compounds were observed under some experimental conditions. However, these experiments are not included with the data reported in Table 1.

It is possible that significant amounts of direct ionization of the organometallic compounds will occur at high sample/methane ratios. The ratio of abundances of parent ions, P^+, to protonated parent ions, PH^+, was substantially independent of experimental conditions for the spectra reported here. For example, the ratio of ions of ^{52}Cr for P^+ and PH^+ from $C_6H_6Cr(CO)_3$, corrected for the natural isotopic abundances of ^{13}C and ^{53}Cr, was constant at 0.340 ± 0.015 as the fraction of ionization from $C_6H_6Cr(CO)_3$ compared with the total ionization from CH_4 and $C_6H_6Cr(CO)_3$ was varied from 0.04 to 0.25. The fraction of ionization from $C_6H_6Cr(CO)_3$ is roughly proportional to the pressure of $C_6H_6Cr(CO)_3$ at a constant pressure of CH_4. Although it is possible that a small amount of P^+ ions in these spectra may be formed by direct electron ionization, the majority of the P^+ ions are produced by ion—molecule reactions.

TABLE 1

CH_4CI MASS SPECTRA OF ARENE-CHROMIUM AND -MOLYBDENUM COMPLEXES

Species or *m/e* •	Sample ionization (%)								
	Benzene	Toluene	Fluoro-benzene	Chloro-benzene	Mesityl-ene	Methyl benzoate	Mesityl-ene—$Mo(CO)_3$	Cyclo-hepta-triene—$Cr(CO)_3$	$(C_6H_6)_2Cr$
Ar—H	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	0.4	
Ar+H	3.0	0.4	0.8	0.8	2.0	1.3	2.0	1.0	4.3
Ar+C_2H_5	1.1	0.2	0.7	0.6	0.4	0.3	0.4	0.2	0.9
$P-\mathrm{Ar}^a$	<0.2	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	1.5
$P\mathrm{H}-\mathrm{Ar}^c$	<0.2	<0.1	<0.3	<0.1	<0.1	ArH	<0.1	<0.1	3.4
$P-3\mathrm{CO}^a$	1.4	1.0	0.8	0.5	1.7	1.7	0.2	0.8	
$P\mathrm{H}-3\mathrm{CO}^a$	0.6	0.7	0.6	0.5	1.0	2.0	0.2	0.8	
$P-2\mathrm{CO}^a$	3.8	2.9	2.6	2.0	2.5	2.2	0.3	2.2	
$P\mathrm{H}-2\mathrm{CO}^a$	2.2	2.3	2.3	2.1	1.4	3.9	0.3	3.6	
$P-\mathrm{CO}^a$	<0.2	0.1	0.4	0.1		<0.1	0.8	1.3	
$P\mathrm{H}-\mathrm{CO}^a$	2.9	0.5	0.3	0.9	0.7	0.7	0.8	5.0	
$P\mathrm{H}-\mathrm{CH_3OH}^a$						5.4			
$P+C_2H_5{}^a$	0.3	<0.1	0.4	0.2	0.1	1.2	0.1	<0.1	<0.05
$P^+/P\mathrm{H}^{+b}$	0.34	0.39	0.32	0.29	0.38	0.41	0.32	0.37	12.9
$(P-\mathrm{H})^c$		⩽0.1			⩽0.1			⩽0.1	
206									3.0
207									1.5
208									59.5
209									19.2
210									4.2
211									0.5
212	1.4								
213	3.2								
214	15.0								
215	47.3								
216	11.4								
217	2.9								
226		1.0						0.8	
227		2.8						2.3	
228		19.1						14.3	
229		52.6						41.1	
230		11.7	1.2					9.9	
231		2.8	3.1					1.8	
232			16.1						
233			52.3						
234			12.0						
235			3.0						
246				0.7					
247				2.3					
248				10.2					
249				36.9					
250				11.0					
251				13.9					
252				3.1					
254					1.0				
255					2.7				
256					17.7				
257					50.3				
258					12.3				
259					2.9				
270						0.9			
271						2.2			
272						16.8			
273						44.2			
274						10.5			
275						2.4			

(continued)

TABLE 1 (Continued)

Species or *m/e*	Sample ionization (%)								
	Benzene	Toluene	Fluorobenzene	Chlorobenzene	Mesitylene	Methyl benzoate	Mesitylene—$Mo(CO)_3$	Cycloheptatriene—$Cr(CO)_3$	$(C_6H_6)_2Cr$
296							2.7		
297							9.1		
298							2.8		
299							8.1		
300							12.9		
301							12.7		
302							11.5		
303							14.6		
304							3.7		
305							5.7		

[a] ^{52}Cr species, corrected for ^{53}Cr and ^{13}C where necessary. [b] Obtained from ratios of ^{52}Cr species after correction for ^{53}Cr and ^{13}C. [c] Estimated residuals for ^{52}Cr species after subtraction of P^+ and PH^+.

Results and discussion

The data are shown in Table 1. The fragment ions have been corrected for interfering isotopes and refer to the ^{52}Cr species. The abundances of ionic species for chlorobenzene include both ^{35}Cl and ^{37}Cl. The values for the ions listed only by mass are the uncorrected averages from a minimum of three experiments. A comparison of these ionic abundances with the abundances of the isotopes of Cr shows that these masses correspond to two species, P^+ and PH^+. Also listed in Table 1 are the ratios of abundances of P^+ and PH^+ ions calculated from ^{52}Cr species, corrected for ^{13}C and ^{53}Cr.

The spectra of the arenechromium carbonyls are generally similar to those reported previously for substituted iron carbonyls [1]. There is, however, significantly less dissociation of the PH^+ ion for the arenechromium carbonyls than was observed for the dieneiron carbonyls [1]. Only the norbornadieneiron carbonyl was reported to have a significant P^+ ion in its CH_4 CI mass spectrum [1], but all of the arenechromium carbonyls show significant molecular ions. The CI spectra show significantly less fragmentation than the corresponding EI spectra [12], for which the most abundant ion is Cr^+. Also absent in the CI spectrum of $C_6H_5FCr(CO)_3$ is the confusing CrF^+ ion present in its EI spectrum [12].

The spectra of the arenechromium carbonyls are virtually identical with respect to species: 80—90% of the sample ionization as P^+ and PH^+; small to negligible amounts of protonated and ethylated arenes; small amounts of loss of one, two and three CO molecules from both PH^+ and P^+; approximately the same ratio of P^+ to PH^+, 0.3 to 0.4; virtually no $(P - H)^+$ ions; little loss of arene to give $Cr(CO)_3^+$; and essentially no $(P + C_2H_5)^+$ ions.

It is essentially impossible to be certain about the site of protonation in any CI study. Because of significant concentrations of protonated ligand ions in the spectra of the dieneiron carbonyl compounds, it was suggested that the compounds are ring-protonated [1]. We feel that the arenechromium carbonyls are metal protonated rather than ring protonated in the gas phase for the following reasons:

(1) Only trivial amounts of protonated and ethylated aromatic ions are produced, and these ions could easily be produced by reactions of CH_5^+ and $C_2H_5^+$ with

free aromatic hydrocarbons. Therefore, there is no indication of ring protonation followed by dissociation.

(2) Although benzene and alkylbenzenes give abundant $(P + H)^+$ and $(P + C_2H_5)^+$ ions in their CH_4 CI-spectra (for several compounds the ratio, $(P + C_2H_5)^+/(P + H)^+$ is about 0.2) [18], the arenechromium carbonyl compounds give very abundant $(P + H)^+$ and negligible $(P + C_2H_5)^+$ ions, $(P + C_2H_5)^+/(P + H)^+ \approx 1\%$.

(3) Although toluene and, to a greater extent, mesitylene have $(P - H)^+$ ions in their CH_4 CI mass spectra, 3% and 12%, respectively, no significant amounts of $(P - H)^+$ ions are observed in the CH_4 CI spectra of the toluene or mesitylene complexes.

The amounts of molecular ions present in the spectra are surprisingly high, $36 \pm 4\%$ of PH^+. For aromatic hydrocarbons, P^+ is roughly 5% of PH^+ [18]. In agreement with previous considerations [1], we attribute these abundant P^+ ions to charge exchange reactions of $C_2H_5^+$ (eqn. 1).

$$C_2H_5^+ + ArCr(CO)_3 \rightarrow ArCr(CO)_3^+ + C_2H_5 \qquad (1)$$

This reaction should be exothermic since the ionization potential of C_2H_5 is 8.4 eV [19] and the ionization potential of $C_6H_6Cr(CO)_3$ is 7.4 eV [20]. Substituent effects are not likely to produce major changes in the ionization potentials of these compounds. Recent measurements suggest a range of 0.4 eV in ionization potentials for the compounds of this study [21].

Only in the case of the methyl benzoate derivative is there strong evidence for protonation away from the metal, since for this compound there is a significant ion (5%) corresponding to $(P + H - CH_3OH)^+$ (eqn. 2). It is significant that

$$(CO)_3CrC_6H_5COOCH_3 \xrightarrow[C_2H_5^+]{CH_5^+} [(CO)_3CrC_6H_5COOHCH_3^+]^\star \rightarrow (CO)_3CrC_6H_5CO^+ + CH_3OH \qquad (2)$$

although there is not much $(P + C_2H_5)^+$, 1.2%, there is more $(P + C_2H_5)^+$ for this compound than for any other compounds of this series. $(P + C_2H_5)^+$ ions are observed in the CH_4 CI spectra of simple esters [22], and the carboxyl group is the most strongly reactive one of the simple functional groups [23].

Also shown in Table 1 is the spectrum of mesitylenemolybdenum tricarbonyl. This spectrum is essentially the same as that for the analogous chromium compound. The differences in the abundances of protonated and ethylated mesitylene are probably not significant with respect to the decomposition of the protonated parent ion. They are probably a reflection of the lower thermal and air stability of the molybdenum complex compared with the chromium compound and result from reactions with the free arenes produced during the sample handling. The generally smaller abundances of ions corresponding to the losses of one, two or three carbonyl groups may indicate a slightly greater stability of the protonated molybdenum than chromium complex. On the basis of these data, one would predict that the analogous Mo compounds would give spectra which contained mostly PH^+ ions, with no significant amounts of fragmentation, and that the P^+/PH^+ ratio would be about 0.3.

Table 1 also gives the CH_4 CI mass spectrum of cycloheptatrienechromium tricarbonyl. This spectrum is very similar to the spectrum of the isomeric toluenechromium tricarbonyl. There are, however, obvious differences in the relative amounts of fragment ions corresponding to the loss of one, two, and three carbonyl groups from these two molecules. The extent of fragmentation is larger for the cycloheptatriene complex than for the toluene complex; therefore, protonated cycloheptatrienechromium tricarbonyl is less stable than its toluene analog.

The EI mass spectra of toluenechromium tricarbonyl and cycloheptatrienechromium tricarbonyl are very similar [12, 13]. Also, the EI spectra of cycloheptatrienetungsten tricarbonyl and toluenetungsten tricarbonyl are very similar, differing primarily in relative abundances of hydrocarbon fragment ions [11].

The CH_4 CI mass spectra of toluene and cycloheptatriene differ markedly in the ratio, $(P - H)^+/(P + H)^+$: 0.06 for toluene and 0.16 for cycloheptatriene. The observation that essentially no $(P - H)^+$ ions are observed for the cycloheptatriene complex again suggests that the attack is predominantly on the metal and not the ring.

The last spectrum reported in Table 1 is that of dibenzenechromium. There is significantly less fragmentation in the CI mass spectrum of this compound than in its EI spectrum [20]. The protonated and ethylated benzene ions may well result from reactions with benzene produced by decomposition from exposure to small amounts of oxygen during sample handling. The unusual characteristic of this spectrum is the very large abundance of P^+ and the low abundance of PH^+, $P^+/PH^+ = 59.4/4.6 = 12.9$*. This very large value should be contrasted with values of 0.3 — 0.4 for the arenechromium tricarbonyls. As was the case with the arenechromium tricarbonyls, there is essentially no $(P + C_2H_5)^+$.

This predominance of P^+ ions in the CH_4 CI spectrum is most unusual [2, 3] and has been noted only once previously, for cobaltocene, for which it was reported that P^+ ions comprised 94% of the additive ionization [1]. Charge exchange with $C_2H_5^+$ has been reported previously [2, 3], but these two observations with $Cr(C_6H_6)_2$ and $Co(C_5H_5)_2$ are the first indications of extensive charge exchange of CH_5^+.

Although one might expect some reduction in the basicity of 'benzene' in this complex compared with free benzene, it would be quite surprising if the proton affinity of the dibenzenechromium molecule were less than that of CH_4, 127 kcal/mole [24]. Protonation does occur as indicated by PH^+ ions, and the existence of $(P + H - C_6H_6)^+$ ions suggests metal protonation followed by decomposition of this compound.

The mechanism of formation of $Cr(C_6H_6)_2^+$ from reaction of CH_5^+ has not been clearly established, but we suggest that shown in eqn. 3. A similar pair of

$$\mathrm{Cr(C_6H_6)_2} \xrightarrow{\mathrm{CH_5^+}} \mathrm{Cr(C_6H_6)_2H^{+\star}} \begin{cases} \longrightarrow \mathrm{Cr(C_6H_6)_2^{+}} + \mathrm{H} & \text{(3a)} \\ \xrightarrow{\mathrm{CH_4}} \mathrm{Cr(C_6H_6)_2H^{+}} & \text{(3b)} \end{cases}$$

reactions would be expected for $Co(C_5H_5)_2$.

The proton affinities (= gas phase basicities) of these compounds are not accurately known at present, but we can estimate that the proton affinities of these compounds will be roughly 180 kcal/mole**. Protonated dibenzenechromium and protonated cobaltocene formed by reaction of CH_5^+, therefore, may be

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*Precise mass measurements were made to confirm these assignments.

**Studies of the proton affinities of these compounds will be reported subsequently elsewhere.

formed with excess energy which may be estimated to be perhaps as high as 53 kcal/mole. Since the ionization potentials of $Cr(C_6H_6)_2$ and $Co(C_5H_5)_2$ are low, 5.7 ± 0.1 eV [20] and 6.1 ± 0.1 eV [20, 25], the decomposition of excited PH^+ ions to these low energy P^+ions is energetically favored and should be very rapid.

The ionization potentials of the arenechromium tricarbonyls should be about 1.5—2 eV (35—45 kcal/mole) higher than the ionization potential of dibenzenechromium [20, 21]. Consequently, the decomposition of PH^+ ions to P^+ ions for these compounds should be less energetically favored and should be slower.

It is worthwhile to compare the gaseous reactions and properties of these organometallic compounds with those observed in solution:

(1) In condensed phases, the bis-arenes are characterized by the lack of reaction on the aromatic rings [26], and for dibenzenechromium we have observed no evidence for attack on the ring by CH_5^+ or $C_2H_5^+$.

(2) In condensed phases, $(C_6H_6)_2Cr$ is readily oxidized to $(C_6H_6)_2Cr^+$, which is stable [26]. The low ionization potential and predominance of $(C_6H_6)_2Cr^+$ in the CH_4 CI spectrum also indicate very great stability for $(C_6H_6)_2Cr^+$. One can consider the formation of $(C_6H_6)_2Cr^+$ from CH_5^+ as oxidation by a strong Bronsted acid. Early results on dibenzenechromium in strong acid gave no evidence for protonation, but did indicate rapid decomposition of dibenzenechromium [27]. Our observations on the relative stabilities of $(C_6H_6)CrH^+$ and $(C_6H_6)_2Cr^+$ would be consistent with solution observations if the dibenzenechromium were oxidized by the strong acids.

(3) Electrophilic attack on the aromatic ligand in the arenechromium tricarbonyl complexes is less than on the free aromatic hydrocarbons [26] in agreement with our observations of much lower abundances of ethyl addition ions for the complexes than for the free aromatic ligands.

(4) The arenechromium tricarbonyls are substantial bases and the benzene-, toluene-, and mesitylene-chromium tricarbonyls have been reported as metal protonated in CF_3COOH [27]. Our gas phase data indicate a substantial basicity for these compounds and suggest that the species are not ring-protonated.

(5) The solution chemistry of dibenzenechromium is characterized by the stability and ease of formation of $(C_6H_6)_2Cr^+$ but similar behavior is not observed for the arenechromium tricarbonyls [26]. The gas phase data on ionization potentials and abundances of P^+ ions in the CH_4 CI spectra also suggest a lower stability and ease of formation of $ArCr(CO)_3^+$ ions.

(6) Although the simple arenechromium tricarbonyls have been reported as metal-protonated in solution [27], reversible keto-protonation is reported if the aromatic ligand contains a carbonyl group (such as benzoic acid) [28]. Our CI spectra show evidence for attack on the ligand only for the methyl benzoate derivative which contains the strongly reactive carboxyl group. Attack on the ligand is indicated in this case by the $(P + H - CH_3OH)^+$ ions, whose analogs were not noted in any of the other spectra.

There are, however, points in which expected similarities of behavior between gas phase and solution data are not observed.

(1) Hydride abstraction from the cycloheptatrienechromium tricarbonyl is readily observed in condensed phases to give a stable cation [26]. Major amounts of $(P - H)^+$ ions were not observed in the CH_4 CI mass spectrum of

cycloheptatrienechromium tricarbonyl in which H^- abstraction by $C_2H_5^+$ might be expected. This difference may be due only to the favorable competition of charge transfer vs. H^- transfer in the gas phase.

(2) It has been reported that in solution the benzyl cation complexed to chromium tricarbonyl is more stable than the free benzyl cation [29, 30]. Since significant amounts of $(P - H)^+$ ions are observed in the CH_4 CI spectrum of mesitylene, 12%, one might reasonably expect significant amounts of $(P - H)^+$ ions in the CH_4 CI spectra of the mesitylene complexes; however, significant amounts of $(P - H)^+$ ions are not observed. This difference may result from the fact that hydride abstraction (H^- transfer) and charge transfer (or oxidation) with mesitylenechromium tricarbonyl are competitive for the gas phase reactant ions but not for the solution species. The differences may also be due to solvation effects.

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