changes in Δg may be achieved by substituting an appropriate radical in a given pair. We consider the case of a benzoyl-^{13}CO radical paired with hydroxybenzyl (pair A), with *p*-bromobenzyl ($g = 2.0047$),[38] and finally with dichloromethyl ($g = 2.0080$, $a_H = -17$ G).[39] The anti-Kaptein net effect discussed for pair A would be even more pronounced for the pair containing the *p*-bromobenzyl radical ($\Delta g = 0.0041$; $G = -5.8$). With dichloromethyl as the second radical, the *g*-factor difference ($\Delta g = 0.0074$; $G = -9.1$) has reached the range where Kaptein's net effect would be obeyed. However, now the multiplet rule would be substantially violated.

Conclusion

The quantitative radical pair theory has been used to define the limits of the qualitative rules introduced by Kaptein for the analysis of CIDNP spectra. The rules are generally valid for net effects if the Δg term is large compared to the hfc's and for multiplet effects if the hfc's are large compared to the Δg term. Deviations from the rules are predicted specifically for multiplets of nuclei A, which are coupled to nuclei X, with larger hfc's. In systems with one large hfc, the ^{13}C CIDNP spectra usually exhibit unexceptional net effects whereas the ^{1}H CIDNP spectra show at least partial multiplet character. The net signal direction or the multiplet phase of these signals deviate from the qualitative sign rules, but they are in good agreement with the quantitative predictions of the radical pair theory. The definition of the range of validity restricts the applications of the rules to some extent but, in exchange, allows them to be used with greater confidence. It is recommended that quantitative simulations be used whenever a radical pair with at least one relatively large hfc is discussed.

Acknowledgment. The authors with to thank Dr. B. Kraeutler for providing a sample of 1,3-diphenylacetone-^{13}CO.

Registry No. 1, 119-53-9; ,1-^{13}CO, 76124-72-6; **1**-^{13}CO,^{13}COH, 53290-42-9; **3**-^{13}CO, 68120-92-3; benzaldehyde, 100-52-7; cyclohexane, 110-82-7; benzaldehyde-^{13}C, 10383-90-1; α-phenylcyclohexylmethanol-d_{11},^{13}COH, 86885-10-1.

---

[38] Closs, G. L.; Paulson, D. R. *J. Am. Chem. Soc.* **1970**, *92*, 2185.

[39] Lehnig, M.; Fischer, H. *Z. Naturforsch. A.* **1970**, *25*, 1963.

Automerization of Gaseous Phenylium Ions. Direct Evidence from the Phenylation of Methyl Halides

Maurizio Speranza,* Yeghis Keheyan, and Giancarlo Angelini

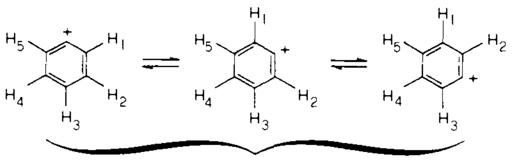
Contribution from the Istituto di Chimica Nucleare del C.N.R., Area della Ricerca di Roma, Rome, Italy.

Received November 8, 1982

Abstract: The reaction of free [^{3}H]phenylium ion, generated from nuclear decay of [p-$^{3}H_2$]benzene in the presence of gaseous methyl halide (CH_3X: X = F, Cl, or Br; partial pressure 30–760 torr), yields the corresponding labeled halobenzenes (F, 32–65%; Cl, 80–90%; Br, 84–91%), together with minor amounts of toluene, halotoluenes, benzyl halides, and fragmentation products. The resulting tritiated halobenzenes are characterized by a significant ^{3}H scrambling over the ring (ortho < meta < para), whose extent increases appreciably when the reaction is carried out at low CH_3X pressures. These results are consistent with related experiments involving the decay of [1,4-$^{3}H_2$]benzene in gaseous CH_3OH (*J. Am. Chem. Soc.* **1982**, *104*, 4773–4780), and are interpreted in terms of a general mechanism involving a relatively fast ($k \simeq 10^7$ s^{-1}) automerization sequence in the [^{3}H]phenylium ion via consecutive 1,2-hydrogen shifts. An alternative interpretation of the CH_3OH data (*J. Am. Chem. Soc.* **1982**, *104*, 3244–3246) can therefore be excluded.

Introduction

The techniques currently available for the production of unsolvated ions of defined structure in both gaseous and condensed phases[1] contribute to the understanding of the *intrinsic* properties of highly reactive species, such as the phenylium ion (**1**),[2] involved as elusive transients in solvolytic reactions.[3] The aptitude of phenylium ion (**1**) to undergo isomerization, in particular, the automerization process (eq 1), has recently received special attention.[2]



(1)

(1)

Observation of the automerization (eq 1) is in contradiction with theoretical predictions of high-energy barriers for process 1, irrespective of the nature of the intermediate species involved ($\Delta E^* = 44$–77 kcal mol^{-1}).[4] Nevertheless, two independent experimental studies[2,5] have been reported recently, whose results are consistent with a relatively fast automerization of phenylium ion (**1**) via consecutive 1,2 hydrogen shifts (eq 1). This conclusion is based essentially upon the fact that, when [p-^{3}H]phenylium ion, (**1**)$_p$, is generated in gaseous methanol (5–65 torr) by the decay of one of the tritium nuclei of [p-$^{3}H_2$]benzene (**2**), the formed tritiated anisole (**4**) exhibits partial ^{3}H reshuffling over the ring positions, in the following order: ortho < meta < para (eq 2).[2]

Occurence of the phenylium ion automerization sequence $(\mathbf{1})_p \rightleftharpoons (\mathbf{1})$ in eq 2 has been recently questioned by Dewar and Reynolds,[6] who attribute the label scrambling, observed in tritiated anisole (**4**), to consecutive hydrogen shifts within the ring-protonated anisoles (**5**) (eq 3). This process supposedly involves multiple crossings over energy barriers whose height is calculated as low as 26–28 kcal mol^{-1}.[6] In this view, the significant isotopic

---

[1] For reviews, see: (a) Cacace, F. *Adv. Phys. Org. Chem.* **1970**, *8*, 79–149. (b) Cacace, F. "Kinetics of Ion Molecule Reactions"; Ausloos, P., Ed.; Plenum Press: New York, 1979. (c) Speranza, M. *Gazz. Chim. Ital.* **1983**, *13*, 37–60.

[2] (a) Speranza, M. *Tetrahedron Lett.* **1980**, *21*, 1983–1986. (b) Angelini, G.; Fornarini, S.; Speranza, M. *J. Am. Chem. Soc.* **1982**, *104*, 4773–4780.

[3] For reviews, see: (a) Ambroz, H. B.; Kemp, J. T. *Chem. Soc. Rev.* **1979**, *8* 353–365. (b) Zollinger, H. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 141–150.

[4] (a) Dill, J. D.; Schleyer, P.v.R.; Binkley, J. S.; Seeger, R.; Pople, J. A.; Haselbach, E. *J. Am. Chem. Soc.* **1976**, *98*, 5428–5431. (b) Castenmiller, W. A. M.; Buck, H. M. *Recl. Trav. Chim. Pays-Bas* **1977**, *96*, 207–213. (c) Krogh-Jespersen, K.; Chandrasekhar, J.; Schleyer, P.v.R. *J. Org. Chem.* **1980**, *45*, 1608–1614. (d) Tasaka, M.; Ogata, M.; Ichikawa, H. *J. Am. Chem. Soc.* **1981**, *103*, 1885–1891.

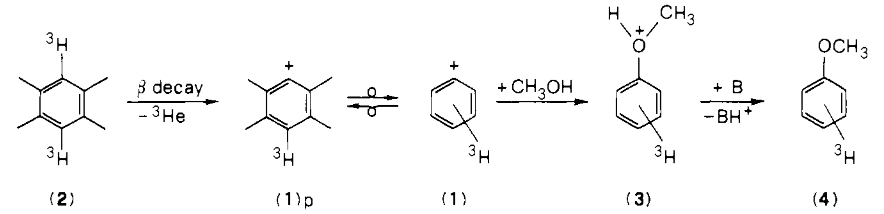
[5] Pollack, S. K.; Hehre, W. J. *Tetrahedron Lett.* **1980**, *21*, 2483–2486.

0002-7863/83/1505-6377$01.50/0

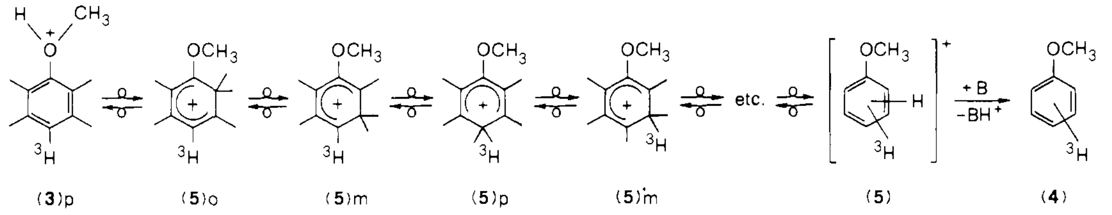
Table I. Tritiated Product Distribution from the Gas-Phase Reaction of Phenylium Ion with Methyl Halides

system composition[a]			relative yields of products[b] (activity, %)				absolute yields[c] (activity, %)
CH_3X		NH_3, torr					
X	torr		C_6H_5X (% p-^{3}H, % m-^{3}H, % o-^{3}H)[d]	$C_6H_5CH_3$	$XC_6H_4CH_3$	$C_6H_5CH_2X$	
F	760	10	65 (94, 3, 3)	10	20	5	47
F	760		37 (93, 5, 2)	32	24	7	61
F	100		32 (90, 7, 3)	40	24	4	39
F	30		45 (81, 15, 4)	31	19	5	35
Cl	760	10	87 (91, 7, 2)	8	3	2	54
Cl	760		90 (91, 5, 4)	2	2	6	50
Cl	100		88 (89, 8, 3)	1	2	9	49
Cl	30		80 (81, 13, 6)	1	2	16	49
Br	760	10	84 (91, 7, 2)	7	3	7	43
Br	760		89 (91, 6, 3)	1	3	7	53
Br	100		91 (89, 9, 2)		1	8	36
Br	30		88 (80, 12, 8)	1	1	10	28
OH	65		94 (80, 15, 5), X = OCH_3; 5, X = OH	1	1		72
OH	55		93 (78, 16, 6), X = OCH_3; 4, X = OH	1	1	1	70
OH	18		85 (76, 17, 7), X = OCH_3; 13, X = OH	1	1	1	65
OH	5		76 (72, 21, 7), X = OCH_3; 19, X = OH	1	3	1	40

[a] The systems contained 1 mCi of $[p\text{-}^3H_2]$benzene (specific activity: 93 mCi $mmol^{-1}$) and O_2 (4 torr), used as a radical scavenger. The decay samples were stored in the dark, at room temperature, for 12–14 months. [b] Expressed as a percentage of the total activity of the aromatic fraction of the tritiated products. Standard deviation of data, ca. 10%. [c] Expressed as the percent ratio of the total activity of the end aromatic products to the activity originally contained in the nuclear-decay formed [^{3}H]phenylium ion reactant. Most of the residual activity is contained in low-boiling fragmentation products. [d] The uncertainty level of the tritium distribution in the ring positions of the labeled halobenzenes is an inverse function of the corresponding positional activity, since this arises from the difference between two activity measurements (see Experimental Section). In general, the uncertainty level ranges around 2–3% for the para position, 20–30% for the meta, and 50–80% for the ortho positions.



(2)



(3)

scrambling we observe in **4** would not conflict with the high-energy barrier calculated for the automerization process 1 in the phenylium ion (**1**). The conceivable occurrence of mechanism 3 in our decay experiments was the subject of accurate evaluation.[2b] However, mechanism 2 lent itself to a suitable explanation of the apparent ^{3}H scrambling in **4** on the grounds of theoretical arguments and specifically designed radiolytic experiments.[7]

We present here additional, compelling evidence against sequence 3 and in favor of the alternative mechanism 2.

This condition has been attained simply by using methyl halides (CH_3X: X = F, Cl, or Br), instead of CH_3OH, as the nucleophilic interceptor of the decay-formed $[p\text{-}^3$Hphenylium ion $(\mathbf{1})_p$ in the gas phase. In this case, attack of the phenylium ions on CH_3X is expected to yield eventually the corresponding tritiated halobenzene with a ^{3}H distribution akin to that of the isomeric ions from the degenerate rearrangement 1. This assertion is based upon the fact that any conceivable ionic intermediate from the gas-phase attack of phenylium ion on CH_3X can hardly undergo fast proton (or tritium) shifts within the aromatic ring, without generating species (e.g., protonated halotoluenes $(\mathbf{7})_p$) which are no longer precursors of the tritiated halobenzene (**8**) (eq 4).

Results and Discussion

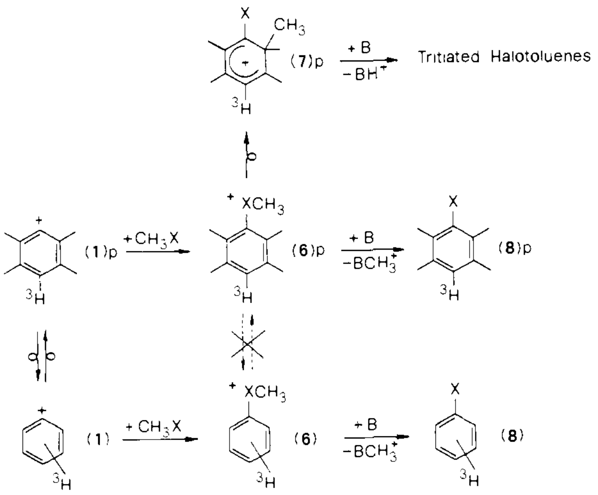
Table I summarizes the experimental evidence: the yields of the identified tritiated aromatics, ^{3}H distribution in the recovered halobenzenes, and the composition of the decay systems. Data from the earlier decay experiments in CH_3OH are included for purposes of comparison. Relatively high yields (28–61%) of tritiated aromatics are formed from the gas-phase attack of singlet[2b] phenylium ion on CH_3X ($-\Delta H°$ = 30–70 kcal mol^{-1}).[8] Most of the residual activity is contained in low-boiling tritiated products, invariably accompanying formation of the aromatic derivatives. Their yield is found to increase upon lowering the

---

(6) Dewar, M. J. S.; Reynolds, C. H. *J. Am. Chem. Soc.* **1982**, *104*, 3244–3246.

(7) The first experimental evidence against mechanism 3 was obtained by generating oxygen-protonated $[p\text{-}^3H]$anisole, $(\mathbf{3})_p$, via gas-phase $CH_3FCH_3^+$ methylation of $[p\text{-}^3H]$phenol, under conditions comparable to those of the CH_3OH decay experiments. The absence of any detectable ^{3}H migration from the para position of the resulting anisole provides circumstantial evidence against mechanism 3 (ref 2b). Dewar's suggestion for experimentally testing mechanism 3 (ref 6) via the protonation $[p\text{-}^3H]$anisole in gaseous methanol is by far less cogent. In fact, any label migration observed in the anisole ring could well arise from the *direct* attack of the gaseous protonating reactant on the para position of the tritiated anisole, without any preliminary coordination on the oxygen atom.

(8) All the conceivable reaction channels leading to the ionic procursors of the tritiated products of Table I are calculated to be from ~30 to ~70 kcal mol^{-1} exothermic, if a heat of formation of 270 kcal mol^{-1} is taken for phenylium ion Rosenstock, H. M.; Larkins, J. T.; Walker, J. A. *Int. J. Mass Spectrom. Ion Phys.* **1973**, *11*, 309–328).



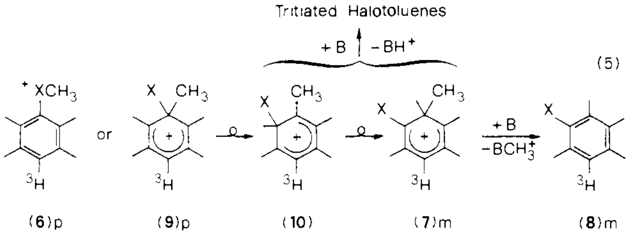
(4)

system pressure, thus suggesting significant fragmentation in the phenylium ion–CH_3X adduct when formed in the absence of efficient collisional deactivation.

The relative composition of the aromatic products is found to depend markedly upon the nature of the halogen atom X involved. In particular, chloro- and bromobenzene are the major products (>80%) from the decay in CH_3Cl and CH_3Br, respectively, whereas almost equal amounts of fluorobenzene (32–45%), toluene (31–40%), and fluorotoluenes (19–24%) are recovered from the CH_3F experiments. Addition of 1.4 mol % of NH_3 (a powerful base B in eq 4) to CH_3F (760 torr) causes tritiated fluorobenzene to become the predominant product (65%). Increase of the relative yield of fluorobenzene in the presence of NH_3 occurs at the expense of toluene and fluorotoluenes, thus suggesting the preliminary formation of a methylphenylfluoronium ion (**6**), which is able to isomerize to **7** or **9** before methyl loss to the base B (eq 4). The same isomerization process appears much less pronounced in the intermediates **6**, when X = Cl or Br. The product distribution of Table I is consistent with the recognized affinity of phenylium ion toward the n electrons of the nucleophilic acceptor, although site discrimination appears less pronounced in the case of CH_3F.

A close correspondence between the ^3H distribution within the halobenzenes and anisole is also evident, which appears governed mainly by the density number of the acceptor and of the additives, rather than by the nature of the nucleophile (CH_3X vs. CH_3OH). These findings indicate that the same mechanism is operative in both CH_3X and CH_3OH decay systems, involving phenylium ion automerization *before* trapping by the nucleophile (eq 2), since other conceivable mechanisms (including the one proposed by Dewar (eq (3)) cannot occur in the CH_3X systems.

It might be argued that the ^3H distribution in halobenzenes **8** may be affected by a conceivable halogen X migration within intermediates $(\mathbf{6})_p$ or $(\mathbf{9})_p$ (eq 5), where the latter is formed from the direct insertion of $(\mathbf{1})_p$ into the C–X bond of CH_3X or by isomerization of $(\mathbf{6})_p$.



(5)

If this were the case, then no appreciable ^3H scrambling should be observable in the fluorobenzene ring, on account of the well-known migratory inaptitude of a F atom in positively charged species, such as $(\mathbf{9})_p$.[9] However, this is contrary to experimental evidence.

Finally, the recognized high mobility of the hydrogen atoms with respect to methyl groups in gaseous arenium ions[10] speaks against the possibility that ^3H scrambling in halobenzenes could arise from multiple methyl group shifts within intermediate $(\mathbf{9})_p$ or $(\mathbf{7})_p$ followed by methyl loss after reaching the para position. The most plausible explanation of the present results, as well as of those concerning the reaction of phenylium ions with CH_3OH, remains sequence 2, that is, a degenerate rearrangement via consecutive 1,2 hydrogen shifts in the phenylium ion (**1**). The automerization competes with the trapping of the cation by a gaseous nucleophile (CH_3X or CH_3OH). Alternative mechanisms are not compatible with the present experimental data.

Automerization 1 of the β-decay-formed phenylium ion (**1**) is allowed by its vibrational excitation, associated inter alia with the relaxation from the regular hexagonal structure of the [1,4-$^3H_2$]benzene precursor to the highly distorted one[4] of the ground-state singlet phenylium daughter ion.[11] In the extreme hypothesis of a phenylium ion formed from [1,4-$^3H_2$]benzene via an adiabatic β^- transition, theoretical calculations set an upper limit of ca. 25 kcal mol^{-1} to its vibrational excitation energy.[4a] This energy is well below the energy barriers ($\Delta E^* = 44$–77 kcal mol^{-1}) theoretically predicted for automerization 1.[4]

It is concluded that a discrepancy clearly remains between the overwhelming experimental evidence of a significant automerization of phenylium ions in the gas state and the high-energy barrier, predicted for the same process, by the currently available results of semiempirical theoretical calculations.

Experimental Section

Materials. The preparation, purification, and isotopic analysis of the [1,4-$^3H_2$]benzene sample used as a source of the decay ions have been described elsewhere.[12] The activity distribution, measured by 213.47-MHz FT ^3H NMR analysis, corresponded to ca. 56% [1,4-$^3H_2$]benzene and ca. 44% [^3H]benzene. Methyl halides, oxygen, and ammonia were high purity gases from Matheson, used without further purification. Merck provided all the research grade aromatic compounds used as carriers or as standards in the gas chromatographic analysis of the decay systems.

Growth of Decay Products. The experimental techniques used for the preparation of the samples are described in full elsewhere.[2] Ca. 1 mCi of the [1,4-$^3H_2$]benzene mixture, diluted with inactive benzene to a specific activity of 93 mCi mmol^{-1}, was introduced into carefully evacuated and outgassed 125-mL Pyrex vessels containing a measured amount of methyl halide together with O_2 (4 torr) used as a radical scavenger. A powerful ion trap (NH_3: 10 torr) was added when required. The vessels were, therefore, sealed off and stored in the dark, at room temperature, for 12–14 months.

Analysis of Products. Two distinct procedures were followed for the analysis of tritiated products from the decay systems. Aliquot portions of the homogeneous samples were subjected to radiogas chromatographic analysis with the main purpose of estimating the absolute yields. A C. Erba Model C gas chromatograph, equipped with a hot-wire detector in series with a 10-mL internal-flow proportional counter, heated at 160 °C, was used for the analyses. The GLC separations were carried out with helium as a carrier gas, the activity of the effluents being monitored by employing a CH_4/He 1:1 counting gas mixture obtained by adding a methane makeup flow to the outlet of the hot-wire detector.

In most cases, the reaction vessels were opened and their contents diluted with precisely known amounts of inactive carriers of interest. After being thoroughly mixed, the samples were subjected to a preparative gas chromatographic separation to resolve and purify each individual component. The recovered fractions were again subjected to

---

[9] (a) Cacace, F.; Speranza, M. *J. Am. Chem. Soc.* **1976**, *98*, 7305–7307. (b) Hehre, W. J.; Hiberty, P. C. *Ibid.*, **1974**, *96*, 7163–7165.

[10] (a) Brouwer, D. M.; Mackor, E. L.; Maclean C. "Carbonium Ions"; Olah, G. A., Schleyer, P.v.R., Eds.; Wiley: New York, 1970; Vol. 2. (b) Brouwer, D. M. *Recl. Trav. Chim. Pays-Bas* **1968**, *87*, 611. (c) Olah, G. A.; Mo, Y. K. *J. Am. Chem. Soc.* **1972**, *94*, 9241–9244. (d) Perez, G. *J. Phys. Chem.* **1976**, *80*, 2983–2987.

[11] Mass spectrometric (Carlson, T. A. *J. Chem. Phys.* **1960**, *32*, 1234–1239) and theoretical studies (Ikuta, S.; Okuno, K., Yoshihara, T.; Shiokawa, T. *Radiochem. Radioanal. Lett.* **1975**, *23*, 213–219. Okuno, K.; Yoshihara, K.; Shiokawa, T. *Radiochim. Acta* **1978**, *25*, 21–25) indicate that phenylium ion **1** is formed from β^- decay in its electronic ground state. Our previous experimental results (ref 2) support a singlet-state electronic configuration for ground-state phenylium ion, in full agreement with the conclusion reached on the grounds of theoretical calculations (ref 4).

[12] Angelini, G.; Speranza, M.; Segre, A. L.; Altman, L. J. *J. Org. Chem.* **1980**, *45*, 3291–3295.

repeated separation and purification steps by preparative GLC, until a constant value of the specific activity of each component, measured by liquid scintillation counting (Tri-Carb 460 C, Packard Instrument Co.) was reached. The yield of each labeled product was deduced from the ratio of its activity to the total activity of the [^{3}H]phenylium ions formed within the system during the storage period, as calculated from the initial activity of [1,4-$^3H_2$]benzene and its known decay rate. The gas chromatographic analyses were carried out with the following columns: (a) Bentone 34–diisodecyl phthalate (1:1 on Chromosorb, W, 1 m) + Carbowax 20 M (15% on Chromosorb W, 3 m), T_c = 60–130 °C; (b) tricresyl phosphate (20% on Chromsorb W-AW-DMCS, 8 m), T_c = 100–120 °C.

Degradation of Tritiated Products. The tritium distribution within the tritiated halobenzenes recovered from the decay samples was determined by a procedure based on the replacement of a ^{3}H of the product by an inactive substituent, followed by the measurement of the corresponding decrease of the molar activity. Substitution reactions were chosen to minimize the danger of label losses or shifts due to unwanted isotopic exchange processes, as demonstrated by blank degradations carried out on suitably deuterated precursors. Chlorination of chlorobenzene carried out in the presence of powdered iron gave a mixture of isomeric dichlorobenzenes which was resolved by preparative GLC on a Bentone 34 column (2 m, 120 °C) and a DC 550 silicone oil column (4 m, 130 °C). The same reaction carried out on fluorobenzene provided *o*- and *p*-chlorofluorobenzene, which were resolved on a Bentone 34 column (2 m, 110 °C) and a tricresyl phosphate column (4 m, 110 °C), and the activity of the purified isomers was measured. The *p*-chlorofluorobenzene was then nitrated (HNO_3/H_2SO_4) and the 2-chloro-5-fluoronitrobenzene was separated with a Bentone 34 column (1 m, 120 °C). Bromobenzene was treated with $Cl_2/AlCl_3$ at 60 °C to give isomeric bromochlorobenzenes which were separated from the starting material with a DC 550 silicone column (2 m, 100 °C). The isomeric bromochlorobenzenes were resolved with a Bentone 34–diisodecyl phthalate 1:1 column (1 m, 110 °C).

Registry No. 1, 82235-88-9; **2**, 73728-29-7; CH_3F, 593-53-3; CH_3Cl, 74-87-3; CH_3Br, 74-83-9; CH_3OH, 67-56-1.

High Resolution Electron Energy Loss Vibrational Studies of CO Coordination to the $(10\bar{1}0)$ Surface of ZnO

K. L. D'Amico,[1a] F. R. McFeely,*[1b] and Edward I. Solomon*[2]

Contribution from the Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, and Department of Chemistry, Stanford University, Stanford, California 94305. *Received May 2, 1983*

Abstract: High Resolution Electron Energy Loss Spectroscopy (HREELS) has been used to study the interaction of CO with the $(10\bar{1}0)$ ZnO surface. The results presented represent the first successful effort to use HREELS to measure the vibrations of CO on any single crystal metal oxide surface and serve as a complement to our earlier photoelectron spectroscopic studies of the CO/ZnO system. Observation of the intraligand C–O stretching mode (273 meV, 2202 cm^{-1}) and its first overtone (539 meV, 4348 cm^{-1}) verify that the CO molecule adsorbed at low coverages under ultrahigh-vacuum (UHV) conditions on $(10\bar{1}0)$ is indeed the same "high frequency" CO observed on ZnO powders. In addition, observation of the Zn–C metal–ligand stretch (31 meV, 250 cm^{-1}) enables application of a normal mode calculation which indicates that the majority of the increased CO stretching frequency is due to an increase in the CO force constant and not just due to mechanical coupling to the surface. These results are discussed in light of the mechanism of methanol synthesis on ZnO.

Introduction

The CO–ZnO system is of significant interest both with respect to its inorganic chemistry and its reactivity. First, zinc oxide is an effective catalyst in taking CO and H_2 to methanol.[3] Further, the CO–ZnO surface complex is rather unusual in that it requires carbon monoxide bonding to a coordinatively unsaturated surface containing metal ions in higher oxidation states surrounded by oxide ligands; this is in contrast to the more usual zero valent metal surfaces where structural analogies to organometallic complexes can be drawn. Associated with this unusual inorganic complex are some rather unusual spectral features which may reflect differences in electronic structure and reactivity. In particular, as opposed to metals where CO binding results in a decrease of the intraligand stretching frequency relative to its gas-phase value due to charge transfer from the metal d orbitals to the $2\pi^*$ orbital on the CO, on ZnO powders the CO stretching frequency increases from 2143 to ~2200 cm^{-1}.[4]

A variety of chemical and spectroscopic studies[5] on four single crystal ZnO Surfaces employing He(II) ultraviolet photoelectron spectroscopy (UPS) have generated the CO binding geometry on the ZnO $(10\bar{1}0)$ surface shown in Figure 1. Here, CO is binding carbon end down approximately along the coordinatively unsaturated Zn direction but tilted somewhat toward the coordinatively unsaturated surface oxide ion. (The unsaturated Zn direction is 19° off normal while the CO has been determined to bind 30° off normal.) A correlation of the geometric structure of the CO–ZnO active site to the electronic structure requires further insight into the vibrational spectrum of this complex. This has been pursued at a single crystal level in ultra high vacuum (UHV) on the $(10\bar{1}0)$ ZnO surface through High Resolution Electron Energy Loss Spectroscopy (HREELS).

In contrast to the wide range of current literature pertaining to HREELS studies of clean and adsorbate covered metal surfaces, there have been relatively few such studies on single crystal metal oxides. Ibach has extensively studied the clean ZnO surface by HREELS, measuring the Fuchs–Kliewer surface phonon spec-

---

[1] (a) Massachusetts Institute of Technology. Presently at Physics Department, Brookhaven National Laboratory, Upton, NY 11973. (b) Massachusetts Institute of Technology. Presently at Thomas J. Watson Research Center, IBM, Yorktown Heights, NY 10598.

[2] Stanford University.

[3] F. Boccuzzi, E. Garrone, A. Zechina, A. Bossi, and M. Camia, *J. Catal.*, **51**, 160 (1978).

[4] A. L. Waddams, "Chemicals from Petroleum", 3rd ed; Wiley, New York, 1973.

[5] (a) R. R. Gay, M. H. Nodine, E. I. Solomon, V. E. Henrich, and H. J. Zeiger, *J. Am. Chem. Soc.*, **102**, 6752 (1980); (b) M. J. Sayers, M. R. McClellan, R. R. Gay, E. I. Solomon, and F. R. McFeely, *Chem. Phys. Lett.*, **75**, 575 (1980); (c) M. R. McClellan, M. Trenary, N. D. Shinn, M. J. Sayers, K. L. D'Amico, E. I. Solomon, and F. R. McFeely, *J. Chem. Phys.*, **74**, 4726 (1981); (d) K. L. D'Amico, M. Trenary, N. D. Shinn, E. I. Solomon, and F. R. McFeely, *J. Am. Chem. Soc.*, **104**, 5102 (1982).

0002-7863/83/1505-6380$01.50/0