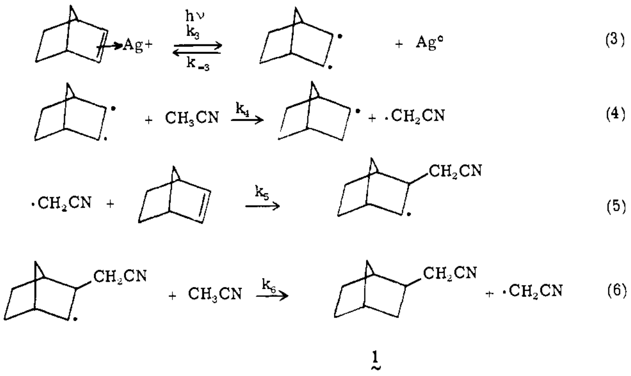
of photoproducts indicated the incorporation of deuterium in products **1** and **2**, but not in **3** or **4**. The generality of this reaction is supported by the observation that propionitrile can be added to norbornene and acetonitrile to several cyclic and acyclic alkenes. The scope of this reaction is under continuing investigation.

The probable mechanism for the formation of photoproduct **1** is given in eq 3–6. In support of photoinitiation via excitation



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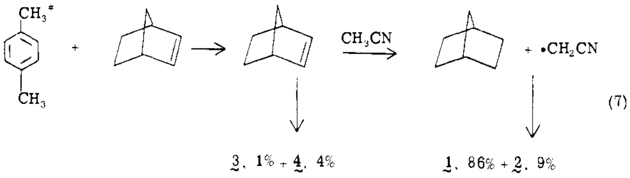
of a ground-state Ag(I)–norbornene complex (k_3), we find that excitation at 313 nm, where the complex is the only absorbing species, effects the formation of **1**–**4**. The quantum yield for formation of **1** is dependent upon norbornene concentration, a linear plot of Φ^{-1} vs. $[\text{norbornene}]^{-1}$ yielding a limiting value of $\Phi = 0.50$. Alkenes which fail to form light-absorbing ground-state complexes do not undergo this reaction. That the mode of excitation may be ligand-to-metal charge transfer is supported by the formation of metallic silver and the nature of the organic products (vide infra). A conceivable alternative role for Ag(I) would be as a catalyst for norbornene singlet → triplet intersystem crossing.[4] Triplet sensitization of norbornene in acetonitrile is known to yield products **1**–**4**[5] (eq 7); however, the product ratios



are different from those obtained in the present Ag(I) initiated reaction (eq 1), and the triplet mechanism would not account for the formation of Ag^0. Moreover, the triplet reaction is quenched by low concentrations of oxygen,[4] whereas the Ag(I) initiated reaction actually requires low concentrations of oxygen (1–5 torr over the solution) and does not occur in thoroughly deoxygenated solutions. Oxygen may react with atomic Ag to yield $Ag^+\,O_2^-$,[6] facilitating chain initiation by preventing back electron transfer (k_{-3}). Oxygen serves as an essential electron carrier in the charge-transfer initiated cyclodimerization of *N*-vinylcarbazole.[7]

Following ligand-to-metal charge transfer, the norbornene cation radical reacts with acetonitrile to form the norbornyl cation and the cyanomethyl radical (eq 4). Hydrogen atom abstraction from acetonitrile by organic cation radicals has been reported by Whitten et al.[8] The reaction of the cyanomethyl radical with norbornene leads to formation of **1** by a free radical chain process (eq 5 and 6). In support of this mechanism, we find that the quantum yield of **1** is substantially reduced in the presence of high oxygen concentrations[9] or acetonitrile-d_3. The solvent isotope effect is consistent with a chain process for the formation of **1**, involving C–D abstraction in both initiation (eq 4) and propagation (eq 6) steps, competing with nonchain processes for the formation of **2**–**4**. Furthermore, when the terminal alkene, 2-ethyl-1-butene, is added to a solution of norbornene and AgOTf, irradiation leads to a mixture of **1** and an acetonitrile adduct of the terminal alkene. Irradiation of 2-ethyl-1-butene and AgOTf under the same conditions gives a substantially lower yield of adduct.

The mechanism of formation of the minor dimeric products **2**–**4** has not received detailed investigation. The Ag(I) initiated (eq 1) and triplet sensitized (eq 7) reactions yield similar dimer ratios **3**:**4** $\sim$ 0.3. In contrast, Salomon and Kochi[10] report a dimer ratio **3**:**4** $>$ 10 for the CuOTf-catalyzed cyclodimerization of norbornene in tetrahydrofuran solution. Furthermore, both Ag(I) initiated and triplet sensitized reactions yield dideuterated **2** in acetonitrile-d_3. Thus it is possible that the formation of minor products **2**–**4** in the Ag(I) initiated reaction occurs via a triplet mechanism. It is interesting to note that norbornene–CuOTf solutions are photostable in acetonitrile, presumably due to strong Cu(I)–nitrile coordination which excludes norbornene activation. Conversely, irradiation of norbornene and Ag(OTf) in tetrahydrofuran leads only to polymerized solvent.[1] Thus the intrinsic coordinative preferences of metal ions are found to impart substantial selectivity in terms of substrate binding and photochemical activation.[11]

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On the Purported Fischer–Tropsch Alkylation of Benzene: Reaction of Benzene with Aluminum Trichloride Revisited

Linda S. Benner, Yee-Hing Lai, and K. Peter C. Vollhardt*

Department of Chemistry, University of California, Berkeley,
and the Materials and Molecular Research Division
Lawrence Berkeley Laboratory
Berkeley, California 94720

Received March 16, 1981

In 1979 it was reported[1] that certain transition-metal carbonyls $M_m(CO)_n$ (M = W, Rh, Ru, Cr, Co) in the presence of $AlCl_3$ catalyzed the so-called Fischer–Tropsch alkylation of benzene. The reaction appears to be of great significance, since it is unprecedented and thought to be homogeneous. However, the fact that no labeling control experiments had been carried out and the assertion that no alkylbenzene formation was observed in the absence of the transition metal, in contrast to the well-established Lewis acid chemistry of benzene,[2-9] prompted a reinvestigation of the reported findings.

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Table I. Product Yields from the Reaction of Benzene and $AlCl_3$ under Various Reaction Conditions

	yield,[a] %		
product	$[AlCl_3]$ = 0.7 M, N_2 (1 atm), 160 °C 48 h	$[AlCl_3]$ = 0.25 M, N_2 (120 atm), 200 °C, 3 h	$[AlCl_3]$ = 0.25 M, 200 °C, 3 h, $[W(CO)_6/\text{diphos}]$,[b] H_2 (100 atm)/CO (20 atm)
toluene	2.187	1.153	1.076 (0.973),[c] (1.134)[d]
ethylbenzene	2.680	1.336	1.660 (1.745),[c] (2.074)[d]
isopropylbenzene	0.182	0.048	0.174 (0.044),[c] (0.137)[d]
n-propylbenzene	0.331	0.090	trace (0.069),[c] (0.012)[d]
butylbenzenes	0.110	0.011	trace (0.021),[c] (0.044)[d]
tetralin	0.726	0.019	0.037 (0.035),[c] (0.050)[d]
phenylcyclohexane	0.059	0.007	0.019 (0.009),[c] (0.034)[d]
biphenyl	1.548	0.081	0.036 (0.129),[c] (0.159)[d]
diphenylmethane	0.228	0.021	5.973 (0.151),[c] (0.562)[d]
diphenylethane(s)	0.340	0.024	0.146 (0.064),[c] (0.280)[d]

[a] GC yield calculated by using *n*-octane as internal standard. These products were characterized by GC/MS and coinjection of authentic samples. Approximately 70–80% of benzene was recovered. [b] $[W(CO)_6]$ = [diphos] = 0.0047 M. [c] Yield from reaction in the absence of $W(CO)_6$. [d] Yield from reaction in the absence of diphos.

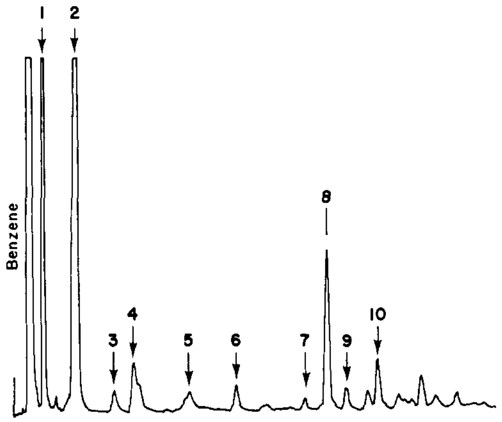

Figure 1. A typical GC trace of the products from the reaction of benzene and $AlCl_3$ ($[AlCl_3]$ = 0.7 M, N_2 (1 atm), 160 °C, 48 h). **1** = toluene, **2** = ethylbenzene, **3** = isopropylbenzene, **4** = *n*-propylbenzene, **5** = butylbenzenes, **6** = tetralin, **7** = phenylcyclohexane, **8** = biphenyl, **9** = diphenylmethane, **10** = 1,2-diphenylethane. **1**–**10** were identified by GC/MS and coinjection of authentic samples. Other minor products were (GC/MS computer library): methyl-, dimethyl-, and ethyltetralins, phenylcyclopentane, fluorene, methyl- and ethylbiphenyl, 1,1-diphenylethane, phenylnaphthalene, and phenyltetralin. Shoulder in peak **4** could not be resolved.

We have found that alkylbenzenes are formed under the previously reported conditions.[1] However, use of D_2 does not give deuterated products. Similarly, application of ^{13}CO does not result in (significant within the error limits of GC/MS) incorporation of the label. Moreover, neither CO or H_2 nor transition metal are necessary for formation of the observed products. Simply heating benzene and $AlCl_3$ in a glass pressure vessel furnishes alkylbenzenes in addition to a variety of other products in rather similar proportions to those observed by using literature[1] conditions (Table I). Application of pressure reduces the number of products (resulting in cleaner GC traces) and their overall yield.[6] A typical GC trace of the reaction of benzene with $AlCl_3$ is shown in Figure 1. Surprisingly, such an analysis of the volatile components of the reaction has never been performed.[7]

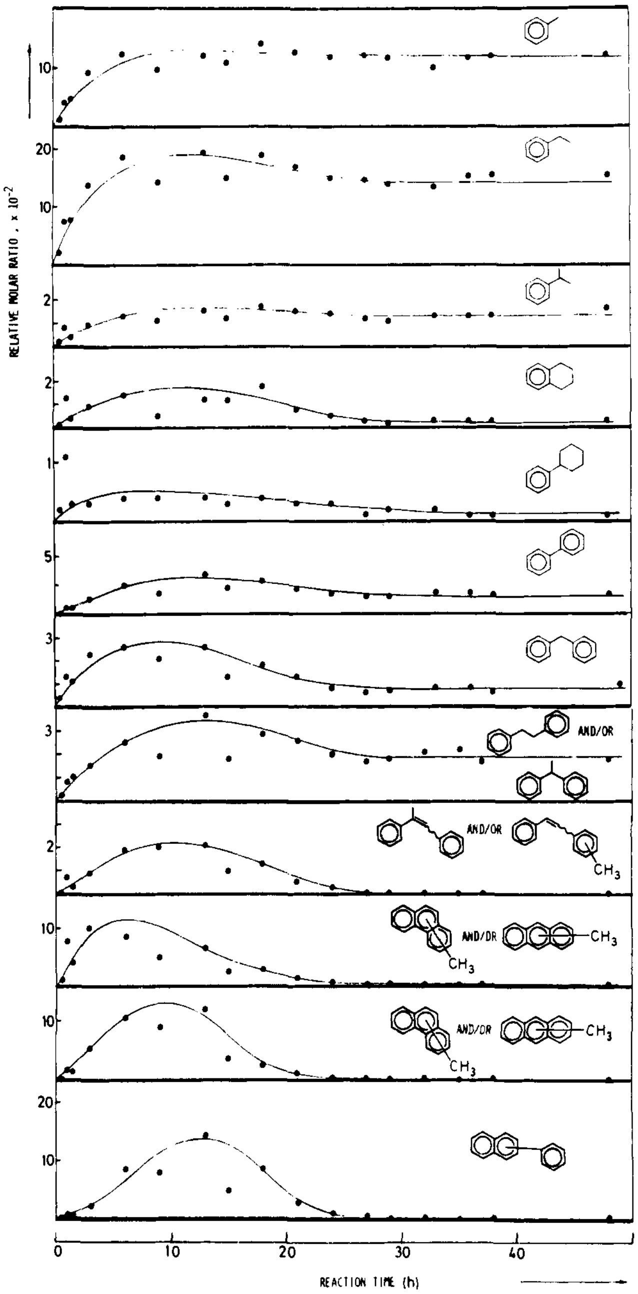

Figure 2. Plot of relative molar ratio of selected products vs. reaction time in the $AlCl_3$/benzene reaction ($[AlCl_3]$ = 0.7 M, N_2 (1 atm), 160 °C, 48 h). *n*-Octane was used as internal standard. Different scales have been used for clarity. Smooth curves are drawn arbitrarily.

In the presence of $W(CO)_6$ (even more so with added diphos) we observe significant amounts of diphenylmethane. Interestingly, the $W(CO)_6$–diphos system furnishes much more isopropyl- than *n*-propylbenzene. Since $AlCl_3$ is a known isomerization catalyst for alkyl groups,[3-10] and its catalytic activity is varied by additives,[11] this result is not surprising. It is also of no consequence to our conclusions. Other Lewis acids such as $FeCl_3$ and

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$AlEt_2(OEt)$ were inactive; $AlEt_2Cl$ was weakly active.

It had been reported[7] that the major product of the reaction of benzene and $AlCl_3$ (0.18 M) at reflux temperature is phenylcyclohexane, and we have confirmed this result. At higher $AlCl_3$ concentration, increasing amounts of alkylbenzenes (mainly toluene and ethylbenzene) are observed, suggesting the possibility that phenylcyclohexane as a primary product undergoes cracking reactions to the observed volatile products. However, at higher temperature the reaction is complicated by condensations, secondary cracking, and catalyst deactivation, most likely by π complexation to higher benzenoids[13] (Figure 2). Such complexation evidently prevents further turnover of benzene and its reaction products. Addition of more $AlCl_3$ leads to a new spurt in benzene turnover. The hydrogen necessary for alkylbenzene production is envisaged to arise via bi- and polyphenyl formation as well as Scholl-type condensation reactions.[3,7,9,10,12] Further evidence for the intermediacy of phenylcyclohexane is derived from the observation of very similar product formation to that depicted in Figure 1 on its reaction with $AlCl_3$.

The major alkylbenzene products are toluene and ethylbenzene. This is consistent with the fact that $AlCl_3$ catalyzes the cleavage of diphenylalkanes to alkylbenzenes[14] and the higher members of the latter are fragmented to the above products.[10] The finding that no xylenes and polysubstituted benzenes are detected is most likely due to the low turnover of the reaction. Thus, such products do appear when toluene and other alkylbenzenes react with $AlCl_3$.

In order to shed further light on the mechanism of the benzene cleavage–hydrogenation process, several additional labeling experiments were run. Reaction of C_6D_6 gave completely labeled products. Not unexpectedly, a 1:1 mixture of C_6H_6 and C_6D_6 gave complete scrambling. Therefore an equimolar mixture of C_6H_6 and $^{13}C_6H_6$ (90% enriched) was exposed to $AlCl_3$ [N_2 (1 atm), 160 °C, 48 h]. Surprisingly, ^{13}C–^{12}C exchange (ca. 5%) is observed in recovered "unreacted" benzene and additional scrambling in all other volatile products[15] as analyzed by GC/MS. Despite this perturbation, the mass spectral peak patterns indicate substantially intact incorporation of alkyl chains derived from the original benzene ring. Thus, the connectivity of the initial carbon arrays is extensively preserved in the alkylbenzenes (including annulated and cycloalkylbenzenes) formed. We do not presently understand the mechanism by which label exchange occurs but suspect it to be independent of the alkylation process.

It might perhaps be emphasized that reactions such as those described in this communication must play a significant role in any process that attempts to liquefy coal in the presence of Lewis acids.[14,16] In any event it appears that the report on the "Fischer–Tropsch alkylation" of benzene should be approached with caution.

Acknowledgment. This work was jointly supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division, and the Assistant Secretary for Fossil Energy, Office of Coal Research, Liquefaction Division of the U.S. Department of Energy under Contract No. W-7405-ENG-48 through the Pittsburgh Energy Technology Center, Pittsburgh, Pa. We thank R. Colborn for a statistical analysis of GC/MS data. K.P.C.V. is a Camille and Henry Dreyfus Teacher Scholar (1978–1983).

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(15) Toluene m/e (% rel intensity): 91 (86.6), 92 (100 normalized), 93 (39.7), 94 (12.4), 95 (16.1), 96 (34), 97 (56.8), 98 (40), 99 (8.7). Ethylbenzene: 105 (28.0), 106 (100), 107 (60.7), 108 (51.2), 109 (10.5), 110 (15.1), 111 (37.2), 112 (50), 113 (28.5), 114 (13.4). *n*-Propylbenzene: 120 (100), 121 (56.1), 122 (46.6), 123 (39.7), 124 (4.67), 125 (24.0), 126 (50.8), 127 (31.5), 128 (26.5), 129 (14.0). *n*-Butylbenzene: 134 (100), 135 (70.9), 136 (56.0), 137 (46.3), 138 (35.9), 139 (26.8), 140 (51.1), 141 (38.0), 142 (28.8), 143 (19.2), 144 (10.1). Attempts to fit these patterns to calculated intensities based on a statistical analysis of the label distribution expected based on the extent of scrambling observed in the recovered benzene gave variable data, always indicating additional but not random scrambling. Similar results were observed for the higher oligophenyls, aromatic systems, and cycloalkylbenzenes.

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Carboxypeptidase A Catalysis of an α,β-Elimination Reaction

Nashaat T. Nashed and E. T. Kaiser*

Department of Chemistry, The University of Chicago
Chicago, Illinois 60637
Received March 6, 1981

We wish to report our finding that carboxypeptidase A (CPA) catalyzes the α,β elimination of a suitably designed ketonic substrate containing in addition to the activated α-methylene group a good leaving group β to the ketone function. In early studies[1,2] CPA was demonstrated to catalyze hydrogen–deuterium exchange with retention of configuration at the activated methylene group of (–)-2-benzyl-3-(*p*-methoxybenzoyl)propionic acid, (–)-**1**, a ketonic analogue of ester and peptide substrates such as *N*-acyl-L-phenylalanines or *O*-acyl-L-β-phenyllactates, respectively. Stereochemical analysis[2] showed that it was the pro-*R* hydrogen of the 3-methylene group of (–)-**1** which undergoes hydrogen–deuterium exchange at the active site of CPA$_\gamma$, and this observation was consistent with the hypothesis that (–)-**1** binds to CPA in a mode similar to that which has been deduced for hydrolytic substrates from X-ray crystallographic studies on peptide–enzyme complexes.[3] Subsequently, an X-ray structure determination[4,5] was reported for the complex of CPA with (–)-**1**, and the arrangement of (–)-**1** at the enzyme's active site was found to be in accord with the binding picture proposed in the stereochemical studies. The γ-carboxylate moiety of Glu-270 is the functional group in the enzyme responsible for the abstraction of the pro-*R* proton from the 3 position of (–)-**1**. With the demonstration in hand that CPA catalyzes stereospecific enolization at the methylene group α to the ketone function in (–)-**1**, a logical step was to ask whether introduction of a good leaving group β to the ketone function would provide a compound susceptible to CPA-catalyzed α,β elimination. To test this possibility, we have synthesized 3-benzoyl-2-[(*p*-nitrophenyl)thio]propionic acid (**2**) and have examined the interaction of carboxypeptidase A with this substrate.

Compound (±)-**2** was obtained by the addition at room temperature of *p*-nitrothiophenol to 3-benzylpropenoic acid (**3**) in acetic acid, employing a catalytic amount of sulfuric acid. Anal. Calcd for $C_{16}H_{13}NO_5S$: C, 57.99; H, 3.96; N, 4.23; S, 9.68. Found: C, 58.08; H, 4.07; N, 4.17; S, 9.50. The ^1H NMR, IR, and mass spectra were consistent with the assigned structure.

Resolution of (±)-**2** was accomplished by repeated recrystallization from acetonitrile of the salt formed between the ethylene ketal of the 3-benzylpropionic acid,[6] (**4**) and enantiomerically pure α-methylbenzylamine. The enantiomers, (–)-**4**, mp 143–145 °C, $\alpha^{25}{}_D$ –31.5° (*c* 2, acetone), and (+)-**4**, mp 144–145 °C, $\alpha^{25}{}_D$ +33.1° (*c* 2, acetone), were obtained by using (–)- and (+)-α-methylbenzylamine, respectively. Treatment of (–)-**4** and (+)-**4** with 10% HCl in acetic acid at room temperature for 2 h gave (–)-**2**, mp 101–102 °C, $\alpha^{25}{}_D$ –108.1° (*c* 1, acetone) and (+)-**2**, mp 103–105 °C, $\alpha^{25}{}_D$ +111.8° (*c* 2, acetone), respectively.

Under conditions usually optimal for the hydrolytic reactions of CPA[7] (0.05 M 4-morpholinopropanesulfonic acid, pH 7.5, 25.0 °C, 3% (v/v) acetonitrile), the enzyme was found to catalyze the

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