# Selectivity in Catalytic Alkyne Cyclotrimerization over Chromium(VI): Kinetic Evaluation Using the Characteristics of Radioactive Carbon-11 Decay for Nondisruptive Ultrasensitive Detection of Adsorbed Species

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The application of carbon-11 to kinetic measurements of molecular sorption is reported using positron annihilation surface detection (PASD). The technique is nondisruptive to dynamic processes and has the sensitivity to detect  $10^{-8}$  of a monolayer. In studies of alkyne cyclotrimerization on silica-alumina-supported Cr(VI), a high selectivity toward p-xylene formation was observed when acetylene-propyne mixtures were cotrimerized at monolayer total alkyne coverages. This selectivity was enhanced to 84% p-xylene, as the partial acetylene coverage was reduced to 1.0% of a monolayer. Competitive sorption studies utilized PASD to measure the surface concentration of [11C]-acetylene coupled with macroscopic sorption measurements of propyne. Surface displacement of sorbed acetylene by propyne was observed with subsequent readsorption. The kinetics of this displacement were evaluated by using PASD in pulse-flow studies with various acetylene and propyne coverages and were modeled to a calculation of the isomeric xylene distribution. A near-identical fit was obtained between experimental and modeled results. This strongly suggested that the observed selectivity for p-xylene formation was due to sorbate interactions resulting in a specific molecular ordering of the alkyne mixture on the catalyst surface.

#### Introduction

Positron-Emitting Radiotracers in Chemical Catalysis. In order to better understand the important dynamic processes occurring on catalyst surfaces, researchers adapted the radiotracer method as a *nondisruptive* means for measuring low concentrations of materials. Unfortunately, the use of radiotracers has been limited to those long-lived, low-energy  $\beta$ -emitting radionuclides which generally could be purchased in some usable chemical form.

Carbon-14 ( $T_{1/2} = 5720$  yr) has perhaps been the most widely used of these radionuclides. Studies of catalytic processes using hydrocarbons tagged with carbon-14 have provided invaluable information on the mechanistic pathways involved in such processes.<sup>1-15</sup> In addition to its utility in mechanistic evaluation, carbon-14 has found use in measurements of adsorption rate and absolute surface coverage.<sup>16-18</sup> Unfortunately, developments in the use of radionuclides like carbon-14 to evaluate the kinetics of a catalytic process have been severely hampered for several reasons.

First,  $\beta$ -counting techniques can only be utilized for sorbate

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measurement, which places constraints on the surfaces which can be probed. This is due to the limited range of a  $\beta$  particle in solid matter. For example, the range of a carbon-14  $\beta$  particle,  $E_{\text{max}}$ = 158 keV, in silicon is approximately  $1.5 \times 10^6$  Å. Therefore, molecular sorption kinetic measurements using low-energy  $\beta$ emitting radionuclides are restricted to the study of single-crystal metal surfaces or, at best, to the outermost layers of supported catalysts. Anomalies may arise when comparing dynamic surface processes between complex supported catalysts and their respective single-crystal metal surface due to the sensitivity of such processes to the structure of the support, as in shape selectivity with zeolite-supported catalysts, and to the support effects on catalyst site activity.

A second problem in using carbon-14 (or any of the long-lived radionuclides) is the trade-off between detection sensitivity of sorbed species and the rapid acquisition of counts relating to dynamic surface phenomena. In a recent paper, Davis et al. described a silicon-barrier detector with a sensitivity to detect 1  $\times$  10<sup>13</sup> molecules cm<sup>-2</sup> containing carbon-14 (equivalent to 1%) of a monolayer of surface coverage).<sup>18</sup> However, the long count periods for acquisition and the low count rates obtained suggest that these radionuclides are not well suited for rapid dynamic kinetic studies. At the expense of sensitivity, increased resolution in dynamic process measurement could be attained, but this might introduce complications in adsorbate surface congestion.<sup>19</sup> For example, 1  $\mu$ Ci of carrier-free carbon-14 would yield ~10 monolayers of coverage on a single-crystal surface  $(1 \text{ cm}^2)$  but would provide only  $1 \times 10^3$  counts s<sup>-1</sup> when the detector described in the Davis work is used. Sorbate interactions in the plurimolecular layers might easily alter the dynamic process one wishes to measure at submonolayer coverage.

It seems obvious that three criteria must be satisfied in ideal kinetic studies in catalysis. Firstly, detection of sorbed molecular species at submonolayer converages should not perturb the process under investigation. While many of the present surface characterization techniques do permit the scrutiny of outermost surface layers with a sensitivity of 1% of a monolayer, they are not suitable for kinetic invesitgations involving rapid processes. This is because these methods may alter the original state of the catalyst or adsorbate during surface detection (via electron, X-ray, or ion bombardment or infrared absorption) and change the steady-state

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conditions of the kinetic phenomenon under investigation. On the other hand, radiotracer detection is nondisruptive because surface or sorbate excitation is not necessary. Secondly, the kinetic process being studied should characterize the entire surface (both inner and outer surfaces) of the real catalyst system. As pointed out earlier, present radiotracer techniques (using low-energy  $\beta$ emitting radionuclides) are restricted to probing surface kinetics on the outermost layers of porous catalysts or single-crystal metal surfaces. Thirdly, the surface detection technique should be capable of resolving continuous changes in the surface process. Again, present radiotracer techniques have shortcomings partly because of the low rate count at low coverage.

The use of molecules labeled with short-lived positron-emitting radionuclides, however, satisfy the above criteria for kinetic investigations in catalysis. This paper reports the use of carbon-11 as one of several radionuclides which have potential use in this regard.

Carbon-11 is an accelerator-generated radionuclide with a 20.4-min half-life which decays through the emission of a 0.99-MeV positron. A number of nuclear reactions have been adapted to appropriate accelerator targets for the generation of this isotope.<sup>20</sup> Carbon-11 possesses a number of favorable characteristics which makes its use amenable to kinetic radiotracer studies in chemical catalysis not possible with long-lived radionuclides.

The emitted positron annihilates upon collision with an electron to yield a coincident pair of 511 keV photons. The solid-support matrix of the catalyst is penetrable by these photons, with some energy attenuation. This permits detection of internal sorbed molecular species in dynamic process studies on real catalyst systems through either single-photon or coincident-photon counting techniques.

The decay rate possible with carbon-11 enables acquisition of data relevant to rapid changes in surface processes. For example, a single-crystal surface covered with 1% of a monolayer of carrier-free carbon-11 would provide  $2.8 \times 10^9$  counts s<sup>-1</sup> (assuming 50% detector efficiency). On the other hand, the same coverage of carrier-free carbon-14 would provide only 1 count s<sup>-1</sup> (assuming the detector efficiency described in the Davis paper<sup>18</sup>).

The incorporation of carbon-11 into molecules of catalytic interest is facilitated by the application of the nuclear recoil technique. At some point after the nuclear event, carbon-11 exists as a kinetically excited neutral atom which eventually reacts chemically with its environment. The outcome of these chemical reactions can be controlled to some extent by alteration of the chemical environment or the degree of excitation of the atom.<sup>21-37</sup>

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The unique advantage of the recoil method is that labeled molecules can generally be prepared at the ultralow concentrations characteristic of the number of nuclear events. A practical catalyst study could be carried out using less than 1  $\mu$ Ci of a carbon-11-labeled molecule. This would amount to less than  $6.5 \times 10^7$ molecules or  $6.5 \times 10^{-8}$  of a monolayer coverage for the above single-crystal surface. The unique ability to measure sorbatesorbate interactions on a near unimolecular scale is possible by this method.

Catalytic Alkyne Cyclotrimerization Chemistry. The field of catalytic alkyne cyclotrimerization chemistry has found application as a powerful tool in radiocarbon dating where conversion of [<sup>14</sup>C]-labeled acetylene-to-benzene facilitates subsequent counting techniques utilized in material dating. Early studies and development of the technique have been described by Leger et al.,38 Tamers,<sup>39</sup> Noakes et al.,<sup>40,41</sup> and Stipp et al.<sup>42</sup> where V(V) activated catalysts were employed. More recent papers by Tamers<sup>43</sup> and Belluomini<sup>44</sup> describe chemical yield optimization in the Ŀ <sup>4</sup>C]-benzene synthesis using Cr(VI) activated catalysts.

We recently reported the adaptation of the above Cr(VI) catalyst to the rapid synthesis of carbon-11 ring-labeled aromatics in high specific activity.<sup>45</sup> This work led to the mechanistic and kinetic evaluation of alkyne cotrimerization chemistry over Cr(VI) using carbon-11 as a radiotracer. The catalytic synthesis of *p*-xylene has potential industrial application to the manufacture of terephthalic acid, a monomer in the production of "Terylene". A more general interest in these processes, however, stems from the ability to convert acetylene into hydrocarbon products that have utility as alternate fuel sources. Processes have been developed for the conversion of methane<sup>46,47</sup> and coal<sup>48,49</sup> to acetylene.

#### **Experimental Section**

Materials. Amorphous silica-alumina (in the form of 2-mm pellets) activated by  $K_2CrO_4$  (0.2% by weight) was used in these trimerization studies. The catalyst is available commerically from Mobil Oil Corp. (type Durahead I) and Kali-Chemie, Hannover, West Germany (type KC Perkator D1). Acetylene, propyne, cyclopropane, and helium (all research grade) were purchased from the Matheson Co. All gases with the exception of helium were further purified on a vacuum line by using conventional degassing techniques.

Benzene and toluene (analytical grade) were obtained from the Mallinckrodt Chemical Co. and used for gas chromatographic calibrations without further purification. The o-, m-, and p-xylenes (minimum; 99 mol % pure) were obtained from Phillips Petroleum Co. and were also used for gas chromatographic calibrations without further purification.

Generation of  $[^{11}C]$ -Alkynes. All irradiations for carbon-11 generation were performed on the Brookhaven National Laboratory 60-in. cyclotron. No-carrier-added (NCA) [11C]-acetylene

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and [11C]-diacetylene were produced by bombarding appropriate hydrocarbon gas targets with a 33-MeV proton beam to induce the  ${}^{12}C(p,pn){}^{11}C$  nuclear transformation. Irradiation samples for the generation of [<sup>11</sup>C]-acetylene were prepared by sealing 300 torr of cyclopropane within a quartz irradiation vessel using standard high-vacuum techniques. Similarly, [11C]-diacetylene was generated from targets containing 100 torr for acetylene. Typical beam intensities were 1  $\mu$ A with exposure times of 100 s. The radiation dose was  $3.48 \times 10^{-4}$  eV molecule<sup>-1</sup>  $\mu$ A<sup>-1</sup> s<sup>-1</sup> as determined by acetylene-to-benzene dosimetry.50 The total gaseous carbon-11 activity was determined by counting an aliquot of the gas in each target using a well-type NaI (T1) scintillation crystal. Both [<sup>11</sup>C]-acetylene and [<sup>11</sup>C]-diacetylene were purified through preparative gas chromatography using a 12-ft Porapak N column (80-100 mesh). Their radiochemical yields were also measured in the usual manner by using gas effluent counting.<sup>51</sup> Polymer activities within the irradiation vessels were measured by washing each vessel in sequence with acetone and methyl alcohol and counting solvent aliquots. The total carbon-11 activity (TA) for each system was taken as the sum of gaseous and nongaseous activities. The radiochemical yield was taken as the ratio of the integrated effluent count to TA, with corrections made for radioactive decay and detector efficiency.

The [<sup>11</sup>C]-acetylene yield generated from the cyclopropane system was measured at 48% TA. The time taken for compound purification subsequent to irradiation limited the amount of activity on hand at the start of a catalyst study. Generally, 5  $\mu$ Ci of [11C]-acetylene was available at the start of each study. In addition to the recoil-labeled [11C]-acetylene, 1.5 µmol of carrier acetylene was also generated. This was attributed to the radiolytic destruction of cyclopropane induced by the incident proton beam. No attempt was made to minimize the radiolytic consequences of the irradiation.

The [<sup>11</sup>C]-diacetylene yield generated from the acetylene system was measured at 39% TA. Less than 0.2  $\mu$ Ci of the compound was available for the catalyst due to the longer time required for column separation during purification. No radiolytic diacetylene was observed within the detection limits of the analytical system.

General Synthetic Procedures. Prior to reaction, 4.3 g of catalyst was placed in a 15-mL-volume Pyrex tube equipped with a vacuum Teflon-type stopcock. The catalyst was heated to 400 °C and evacuated for 1 h to rid the surface of sorbed water. (After reaction, the catalyst could be reactivated by flowing oxygen over the heated catalyst at 400-500 °C for 1 h). Reactants were introduced cryogenically at monolayer coverages. A monolayer coverage ( $\theta = 1$ ) corresponded to three sorbed molecules per chromium site on the support as determined from a previous saturation coverage study.45

At this point, the reaction tube was sealed and warmed to ambient temperature where reaction was allowed to ensue. After 20 min, products were desorbed from the catalyst by first opening the reaction tube to an evacuated U-trap submerged in liquid nitrogen and then by heating the catalyst to 225 °C. Vacuum cross-pumping through the U-trap was employed to aid in product transfer. In all studies, the total desorption time used was 10 min. The time parameters employed were reported in an earlier paper describing optimized experimental conditions.45

Product Analysis. All product analyses were carried out using a radio gas chromatograph equipped with a thermal conductivity response detector and a Wolf flow-through gas proportional counter.52 A major modification to the standard radio gas chromatograph was the inclusion of an effluent combustion tube at the column outlet.<sup>53,54</sup> This combustion tube was constructed from 0.2-in.-i.d. quartz tubing and filled with oxidized copper wool. The catalyst was operated at 800 °C to optimize combustion. Carbon-11-labeled compounds were quantitatively oxidized to

Adsorption Measurement Apparatus



Figure 1. Block diagram of static catalyst reactor with pressure and surface  $\gamma$  detectors.

 $^{11}CO_2$  and H<sub>2</sub>O. Water was removed through sorption on a magnesium perchlorate trap located in the exit end of the combustion tube, and the <sup>11</sup>CO<sub>2</sub> radioactivity was measured in the flow-through gas proportional counter.

When a mixture of acetylene and propyne was added to [<sup>11</sup>C]-acetylene prior to catalytic reaction, five carbon-11-labeled aromatic products were generated (benzene, toluene, xylenes) from mixed acetylene-propyne trimerization. (Trimethylbenzene was also generated from pure propyne trimerization but was not carbon-11 labeled since [<sup>11</sup>C]-acetylene was the only source of the label.) The distribution of the carbon-11-labeled products as a function of acetylene-propyne mole fraction was reported previously.<sup>45</sup> The variation in the  $[^{11}C]$ -xylene isomer distribution is reported in this paper. The  $[^{11}C]$ -xylenes were identified by coinjection of authentic samples on three columns: (i) a 16-ft column of 20% SE-30 on 50-80-mesh Anakrom ABS operated at 120 °C; (ii) a 20-ft column of 30% 1,2,3-tris(2-cyanoethoxy)propane on 80-100-mesh Chromosorb P operated at 120 °C; and (iii) a 12-ft column of 5% Bentone 34 + 5% diisodecylphthalate on 60-80-mesh Chromosorb P temperature programmed from 80 to 120 °C at a rate of 5 °C min<sup>-1</sup>. The first two columns permitted resolution of o-xylene from p- and m-xylenes, whereas the third column allowed for complete resolution of the three isomers.

The reaction of acetylene with [<sup>11</sup>C]-diacetylene was of interest to probe adsorbate surface orientation. Three columns were used to separate [<sup>11</sup>C]-biphenyl- and [<sup>11</sup>C]-phenylacetylene during product analysis: (i) a 6-ft column of 20% SE-30 on 50-80-mesh Anakrom ABS operated at 160 °C; (ii) a 10-ft column of 30% 1,2,3-tris(2-cyanoethoxy)propane on 80-100-mesh Chromosorb P operated at 150 °C; and (iii) a 10-ft column of 10% Apiezon L grease on 80-100-mesh Chromosorb P operated at 120 °C.

Sorption Apparatus. Figure 1 illustrates a block diagram of the reactor, detectors, and peripheral electronics utilized in static sorption studies of acetylene and propyne. The reactor was constructed of Pyrex glass with stainless-steel connectors and high-temperature Teflon-type vacuum stopcocks. The reactor was maintained at ambient temperature during sorption. The main catalyst chamber was fixed within a 100-mm-diameter lead cylinder with 35-mm-thick walls. An 8-mm hole in the bottom of the cylinder was used to collimate the detection zone of a 76.2  $\times$  76.2 mm well-type NaI (T1) scintillation crystal. The NaI (T1) detector normally possessed a 57.7% efficiency for 511 keV photons in an uncollimated state, but this decreased to 3.2% when collimation was in place.

After purification, [11C]-acetylene was cocondensed in vacuo into the side storage bulb of the reactor with an appropriate amount of carrier alkyne. The gases were warmed to ambient temperature and then introduced simultaneously to the evacuated chamber containing 4.3 g of active catalyst. A Barocel electronic manometer provided continuous measurement of the alkyne pressure drop which was equated to the percent uptake of alkyne

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Figure 2. (a) Sorption of carrier acetylene vs. elapsed time of exposure to Cr(VI) catalyst for coverage of 0.83 ( $\Delta$ ), 2.9 ( $\oplus$ ), and 9.0 (O). (b) Sorption of [<sup>11</sup>C]-acetylene vs. elapsed time of exposure to Cr(VI) for carrier coverages of 0.83 ( $\Delta$ ), 2.9 ( $\oplus$ ), and 9.0 (O).

on the catalyst surface. Corrections were made for initial volume equilibration using the measured pressure drop for inactive catalyst (no sorption took place under these conditions). Simultaneously, the NaI (T1) detector measured the increase in surface carbon-11 as sorbed  $[^{11}C]$ -acetylene. This was also equated to a percent uptake on the basis of the known amount of carbon-11 at the beginning of the study.

In preliminary tests designed to ascertain the reliability of carbon-11 data related to surface concentration,  $2-\mu$ Ci samples of [<sup>11</sup>C]-acetylene were diluted to three specific activities to yield surface coverages of 0.8, 2.9, and 9.0. Comparisons were made in the dynamic uptake of [<sup>11</sup>C]-acetylene and unlabeled acetylene over 4.3 g of the catalyst. A comparison of the results from the three dynamic uptake studies can be seen in Figure 2a,b, where the percent uptake was plotted as a function of catalyst exposure time. The percent uptake was measured relative to the original number of molecules of acetylene and [<sup>11</sup>C]-acetylene in the gas chamber. Results indicated identical correlation between the uptake of [<sup>11</sup>C]-acetylene and unlabeled acetylene.

In catalyst studies aimed at assessing the kinetics of sorption and surface displacement, a dynamic pulsed-flow reactor was constructed. Pulses of alkyne were injected into a helium sweep (30 mL min<sup>-1</sup>) which carried the pulse into the catalyst bed of the reactor. Fritted ceramic disks were fixed above and below the catalyst bed to diffuse the pulse passing through the catalyst in order to prevent molecular channeling. The inlet and outlet ports from the main chamber were equipped with thermal conductivity sensors. The differential signal output provided a measure of the amount of the pulse which remained sorbed on the catalyst. Radiation detection and peripheral counting electronics were identical with what was used in the static reactor studies for surface carbon-11 measurements.

The kinetics for surface acetylene displacement by propyne were assessed by sequencing the pulses of  $[^{11}C]$ -acetylene and propyne. The decrease in surface  $[^{11}C]$ -acetylene was measured during the propyne pulse as a function of propyne coverage and also as a function of original surface acetylene coverage for fixed propyne pulses.

### **Results and Discussion**

Selectivity for p-Xylene Formation. In present studies, enhanced selectivity was observed for  $[^{11}C]$ -p-xylene formation from acetylene-propyne cotrimerization chemistry on Cr(VI). Results presented in Figure 3 illustrate the distribution of  $[^{11}C]$ -xylene isomers as a function of acetylene and propyne mole fractions at monolayer coverages. The  $[^{11}C]$ -p-xylene distribution increased to 84% as the acetylene carrier mole fraction was decreased to zero. Zero mole fraction of acetylene actually corresponded to a surface coverage of 0.01 relative to a propyne coverage of 0.99. The trace amount of radiolytic acetylene generated along with  $[^{11}C]$ -acetylene accounted for this. Over the same range, a



Figure 3. Effect of carrier alkyne mole fraction on the  $[^{11}C]$ -xylene product distribution.



Figure 4. Surface interaction of alkynes at Cr(VI) site.

corresponding decrease in the  $[^{11}C]$ -*m*- and  $[^{11}C]$ -*o*-xylene distribution was also observed.

Selectivity and Molecular Orientation on Cr(VI). In subsequent studies, the effect of adsorbate surface orientation on catalyst selectivity for *p*-xylene formation was considered. In probing this question with carbon-11, it is possible to consider sorbate surface orientation in a totally noncongested state of the surface. The problem was to design the adsorbate structure such that two reaction pathways (distinguishable by their products) would characterize axial and coaxial orientation of the adsorbate. Diacetylene fit the criteria of the study. Axial sorbate orientation along the plane of the surface would provide two active sites for trimerization to yield biphenyl. On the other hand, coaxial sorbate orientation would place the molecular axis perpendicular to the plane of the surface and provide only one active site to yield phenylacetylene. [11C]-Diacetylene was prepared under no-carrier-added conditions via recoil labeling as previously described. Noncongested surface orientation of  $[^{11}\hat{C}]$ -Diacetylene in a monolayer of acetylene yielded only [11C]-phenylacetylene from the subsequent cotrimerization surface chemistry. This suggested coaxial surface orientation, at least in the noncongested state.

In view of the above results, random coaxial orientation of an unsymmetrical alkyne like propyne at its  $C_1$  or  $C_2$  position would not account for the observed catalyst selectivity. Studies using monolayer coverages of pure propyne yielded a 4:1 distribution of 1,2,4-trimethylbenzene to 1,3,5-trimethylbenzene. A random ordering of coaxially oriented propyne molecules on the surface would have yielded, at best, a 3:1 distribution of the isomers. This ordering of alkyne molecules assumes that stepwise molecular sorption occurs at a single chromium site. Sorption of the third alkyne molecule at the catalyst site prior to trimerization may actually proceed via a gas-surface interaction with the previously sorbed alkyne molecules. This interaction may be enhanced through radical interactions of the sorbed molecules with nonsorbed species in the near vicinity of the surface as depicted in Figure 4.

While sorbate orientation may, in part, contribute to the selectivity of the surface chemistry for the single-component propyne system, it does not suffice to explain the selectivity for *p*-xylene formation in the acetylene-propyne system and the dependence of this selectivity on the relative distribution of adsorbates.



Figure 5. Competitive sorption of propyne ( $\bullet$ ) and no-carrier-added [<sup>11</sup>C]-acetylene (O) at propyne coverages of (a) 0.95, (b) 3.35, and (c) 9.00.



Figure 6. Surface displacement of  $[^{11}C]$ -acetylene (O) by propyne sorption ( $\bullet$ ) at coverage 3.35 for surface acetylene coverages of (a) 0.01, (b) 0.62, and (c) 1.69.

However, sorbate surface order and orientation in the acetylene-propyne system may be strongly dependent on dynamic surface phenomena such as competitive sorption.

Competitive Sorption of  $[^{11}C]$ -Acetylene and Propyne. Results from the competitive sorption of unlabeled propyne (at coverages of 0.95, 3.35, and 9.0) and NCA  $[^{11}C]$ -acetylene (at coverage 0.01) were presented as percent of uptake vs. time in parts a-c of Figure 5 for the three coverages of propyne, respectively. The uptake of propyne on the catalyst was independent of coverage. This was in contrast to what was observed in the acetylene uptake curves in Figure 2a for comparable coverages. Also,  $[^{11}C]$ -acetylene was physically displaced by propyne from the detection zone of the catalyst and then later adsorbed in the plurimolecular layers of surface propyne. This displacement was enhanced for propyne coverages between 0.69 and 3.35 but was suppressed at the higher coverage of 9.0. At the high coverage of 9.0, propyne may actually "cage" the displaced  $[^{11}C]$ -acetylene in the multilayers and prevent its diffusion out of the detection zone.

The sorption of  $[^{11}C]$ -acetylene and propyne was sequenced to determine whether displaced  $[^{11}C]$ -acetylene was actually sorbed species or gaseous molecules in close proximity to the surface to allow detection. The change in surface concentration of preadsorbed  $[^{11}C]$ -acetylene was measured as a function of propyne sorption in the dynamic mode. Results illustrated in Figure 6a indicated a physical displacement of sorbed  $[^{11}C]$ -acetylene by propyne during the first 5 min of propyne exposure for three monolayer coverage capability. Readsorption of  $[^{11}C]$ -acetylene was also observed, once the surface was saturated with propyne.



Figure 7. Sequence of  $[^{11}C]$ -acetylene-propyne surface interactions to yield  $[^{11}C]$ -*p*-xylene.

The displacement-readsorption sequence was independent of the time [<sup>11</sup>C]-acetylene was allowed to remain on the surface prior to propyne exposure. The sequence was also independent of surface congestion with macroscopic acetylene at coverage  $\theta = 0.62$  as indicated in Figure 6b. However, once a monolayer of acetylene was established on the surface, no displacement was observed as indicated in Figure 6c. This could be attributed to initiation of trimerizing surface chemistry.

The displacement of sorbed acetylene by propyne may be due to differences in the sorbed states of each of these species. The drastic differences in the sorbate uptake curves for similar coverages of acetylene and propyne lend support to this argument. However, the assessment of these sorbed states through thermal desorption spectroscopy (TDS) was not addressed in the present study.

The qualitative picture involving [<sup>11</sup>C]-acetylene adsorption, displacement by propyne, and readsorption lends itself to the hypothesis that the mechanism for selective [<sup>11</sup>C]-p-xylene formation is dependent on these dynamic surface phenomena. The scheme presented in Figure 7 illustrates this point. In presenting this scheme, several assumptions had to be made. First, the fraction of [<sup>11</sup>C]-acetylene displaced must be substantial. This magnitude could not be assessed from the static reactor measurements since displacement and readsorption are likely to proceed simultaneously. However, this assumption is justified by other data (vide infra) presented in this paper. Second, surface congestion by propyne results in an ordering of coaxially oriented molecules fixed at the  $C_1$  position. Coaxial alkyne orientation was justified from the [<sup>11</sup>C]-diacetylene studies. Also, pure propyne trimerization studies indicated preferred fixation at either  $C_1$  or  $C_2$ . The scheme, however, depicts propyne fixation at a preferred  $C_1$  site due to steric hindrance by the methyl group. Previous studies have indicated that the chemical reactivity of propyne relative to that of acetylene for surface trimerization was 0.8.45 This decreased reactivity was attributed to the hampered ability of the  $C_2$  site of propyne to surface bond. This premise carried over into subsequent studies where 2-butyne and acetylene were cotrimerized. The chemical reactivity of 2-butyne relative to that of acetylene was measured at 0.1.55 When both alkyne



Figure 8. Sequence of  $[^{11}C]$ -acetylene-propyne surface interactions to yield  $[^{11}C]$ -o- and  $[^{11}C]$ -m-xylenes.



Figure 9. Plot of the  $[^{11}C]$ -acetylene surface concentration  $[A]_s$  as a function of tme for various propyne coverages.

sites are blocked, its reactivity was severely limited. In the readsorption of  $[^{11}C]$ -acetylene, a third assumption is made that this process occurs via gas-surface interactions with sorbed propyne. One could argue that the enhanced readsorption rate of  $[^{11}C]$ -acetylene with increased propyne surface coverage may be due to its increased sticking probability with surface propyne radicals.

Given the above set of conditions for molecular ordering and orientation on the catalyst,  $[^{11}C]$ -*p*-xylene could be expected to be formed. On the other hand, a decrease in  $[^{11}C]$ -acetylene displacement might lend itself to higher ortho and meta isomers through the scheme presented in Figure 8. The observed increase in  $[^{11}C]$ -*o*- and  $[^{11}C]$ -*m*-xylenes with increasing proportions of acetylene-to-propyne carrier suggested that the  $[^{11}C]$ -acetylene displacement rate was sensitive to changes in the acetylene and propyne coverages.

Kinetic Evaluation of  $[{}^{11}C]$ -Acetylene Displacement by Propyne from Cr(VI). In order to evaluate the kinetics of  $[{}^{11}C]$ -acetylene displacement, two studies were performed in a dynamic reactor where the change in the sorbed  $[{}^{11}C]$ -acetylene concentration was measured as a function of (i) propyne coverage at a fixed acetylene coverage of 0.01 and (ii) acetylene coverage at a fixed propyne coverage of 0.28. Since the rates of alkyne diffusion to and away from the catalyst surface are not limiting in the pulsed fast-flow reactor design, the rate of change in surface  $[{}^{11}C]$ -acetylene



**Figure 10.** Kinetic plot of  $[^{11}C]$ -acetylene displacement rate at constant initial coverage ( $\theta$ ) of 0.01 for various propyne coverages.

concentration would characterize the kinetics of displacement. Results of the first study are presented in Figure 9 for propyne coverages of 0.1, 0.28, 0.57, 0.83, and 1.0. Higher coverages were not studied since the original selectivity measurements for <sup>[11</sup>C]-*p*-xylene formation were taken at coverages not greater than 1.0. In all cases, the propyne pulse was introduced into the helium sweep after 180 s elapsed from the zero time. The zero time was arbitrarily set when the carbon-11 activity from the [<sup>11</sup>C]-acetylene pulse equilibrated in the catalyst chamber. Displacement of [<sup>11</sup>C]-acetylene was observed only when a propyne pulse was introduced. In addition, analysis of the catalyst effluent by radio gas chromatography indicated that the displaced carbon-11 activity was indeed [<sup>11</sup>C]-acetylene. The kinetic dependence on the fast-flow parameter was tested by increasing the helium flow 5-fold. No change was observed in the kinetics of the displacement.

In evaluating the kinetics of the displacement reaction, the logarithm of the [<sup>11</sup>C]-acetylene surface concentration, log [A]<sub>s</sub>, was plotted as a function of time and was presented in Figure 10. A linear correlation of the data was obtained for propyne coverages at or above 0.28. This indicated that the displacement kinetics showed a first-order dependence on the surface acetylene concentration at these propyne coverages. However, the data yielded a nonlinear fit at the lower 0.1 propyne coverage. For a coverage of 0.28, nearly every Cr site would contain a sorbed propyne molecule. A 0.1 propyne coverage would leave  $\sim 70\%$  of the Cr sites vacant. These vacant sites have the potential to readsorb displaced [<sup>11</sup>C]-acetylene and cause a deviation in the first-order dependence of the displacement kinetics.

In addition, the displacement rate of  $[^{11}C]$ -acetylene may be limited by the translational surface diffusivity rate of propyne. Two facts support the premise that propyne surface diffusion occurs. The displacement rate showed a second-order dependence on the surface propyne concentration between 0.28 and 1.0 coverages. This was apparent by the linear correlation obtained in Figure 11 from a plot of the absolute value of the slope, S, from the data in Figure 10, as a function of the square of the propyne coverage,  $\theta_p^2$ . The second-order dependence observed at near unit Cr site coverage by propyne ( $\theta = 0.28$ ) suggested that aggregation of surface propyne had occurred either during initial sorption or as a result of surface diffusion. Secondly, the surface [<sup>11</sup>C]acetylene plot in Figure 9 showed nearly 60% displacement with only 30% Cr-site coverage by propyne ( $\theta = 0.10$ ). For such low coverages of propyne, localized sorption can not achieve this degree of acetylene displacement.

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Figure 11. Second-order dependence of the acetylene displacement rate on propyne coverage  $(\theta)$ .



**Figure 12.** Kinetic plot of  $[^{11}C]$ -acetylene displacement rate at various initial acetylene coverages for a constant propyne coverage of 0.28.

In the second study, the kinetics of  $[^{11}C]$ -acetylene displacement were evaluated for acetylene coverages of 0.01, 0.07, 0.37, and 0.67. The propyne pulse was held constant at a coverage of 0.28. Results from this study are presented in Figure 12 as the logarithm of the  $[^{11}C]$ -acetylene surface concentration, log  $[A]_{s}$ , vs. time. The linear correlation observed in all cases indicated that the first-order dependence of the displacement rate was maintained at least for submonolayer acetylene coverages.

Catalyst Selectivity Dependence Modeled to the Relative  $[^{11}C]$ -Acetylene Displacement Rate. It was possible to quantitate the model, supported by Figure 1, for the dependence of  $[^{11}C]$ -p-xylene production on  $[^{11}C]$ -acetylene surface displacement. In doing so, it was necessary to first correlate the rate of this displacement process to both acetylene and propyne coverages. The slopes of the lines in Figure 10 were normalized relative to the data obtained from a propyne coverage of 1.0 and plotted as the normalized rate of displacement vs. propyne coverage in Figure 13. In a similar fashion, the slopes of the lines in Figure 12 were normalized relative to the data obtained from an acetylene cov-



**Figure 13.** Plot of the normalized  $[^{11}C]$ -acetylene displacement rate as a function of the individual acetylene coverage (O), the individual propyne coverage ( $\bigcirc$ ), and the cumulative effect of both alkynes being present on the surface (solid line).



Figure 14. Modeled  $[^{11}C]$ -xylene distributions (para ( $\bullet$ ), meta (O), ortho ( $\Delta$ )) as a function of alkyne carrier mole fraction overlaid with experimentally measured distributions (dotted lines).

erage of 0.01 and were also plotted in Figure 13 as normalized displacement rate vs. acetylene coverage. The net effect of these two traces is depicted in Figure 13 by the solid line. As the acetylene-propyne coverage distribution was varied from 0.01-1.0 to 0.7-0.3, the net displacement rate decreased nonlinearly by 32%. This plot was applied to the calculation of the [<sup>11</sup>C]-xylene distribution using the experimental distribution observed for acetylene-propyne carrier mole fractions of 0-1.0 as a data base. The product of the relative displacement rate, taken for 0.1 incremental changes in the sorbate coverages, and the [<sup>11</sup>C]-*p*-xylene distribution measured at the data base (84%) yielded a modeled [<sup>11</sup>C]-*p*-xylene percent distribution. The remaining percentage that this isomer distribution depended only on the steric inhibition

of a gaseous propyne molecule when interacting at a Cr site containing cosorbed propyne and acetylene molecules. This distribution was measured as 17% and 83% o- and m-xylene, respectively.

Results from the above calculation are presented in Figure 14. For comparison, the experimental data from Figure 2 are overlaid as dashed lines in Figure 14. The nearly exact fit between the modeled and experimental yields indicated that the observed selectivity in the Cr catalyst was indeed dependent on the extent of acetylene-propyne adsorbate interaction resulting in physical displacement of acetylene from the site.

#### Conclusions

The feasibility of using short-lived positron-emitting radionuclides such as carbon-11 in kinetic investigations on catalyst surfaces was demonstrated in the kinetic evaluation of acetylene-propyne adsorbate interactions which resulted in specific molecular order and orientation on a Cr(VI) catalyst. This catalyst yielded a high selectivity for *p*-xylene formation in the surface cotrimerization of acetylene and propyne. The selectivity was altered at monolayer alkyne coverages through variation of the acetylene-propyne distribution. Cosorption studies with  $[^{11}C]$ - acetylene and propyne indicated that acetylene was physically displaced from the Cr site by sorbing propyne molecules. The rate of this displacement was measured and found to increase in a second-order dependence with increasing propyne coverage and increase in a first-order dependence with increasing acetylene coverage. Results also suggested that the displacement rate was limited by the surface migration rate of sorbed propyne. Readsorption of displaced [11C]-acetylene onto coaxially oriented surface propyne, Cr bound at the  $C_1$  position, was also observed. This readsorption process was likely to proceed via reactive gas-surface interactions. Calculation of modeled xylene yields as a function of the acetylene displacement rate resulted in distribution curves which were nearly identical with experimental data. This demonstrated the sensitivity of this particular catalyst's selectivity to dynamic nonchemical adsorbate-adsorbate interactions.

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## Electronic Spectra of Benzoic Acid in a Supersonic Free Jet

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The fluorescence excitation, dispersed fluorescence, and multiphoton ionization spectra of benzoic acid have been measured in a supersonic free jet. We found for the first time a nonfluorescent  ${}^1(n,\pi^*)$  state for the benzoic acid dimer by the multiphoton ionization technique. The  ${}^1(n,\pi^*)$  state of the isolated dimer is the lowest excited singlet state (S<sub>1</sub>), and it is located at 665 cm<sup>-1</sup> below the fluorescent S<sub>2</sub>( $\pi,\pi^*$ ) state. The emissive character of the S<sub>2</sub>( $\pi,\pi^*$ ) state results from a small rate of internal conversion to the S<sub>1</sub>( $n,\pi^*$ ) state. Intramolecular vibrational relaxation (IVR) within the S<sub>2</sub>( $\pi,\pi^*$ ) state of the dimer is discussed on the basis of the dispersed fluorescence spectra. The IVR rate is rather slow compared with hydrogen-bonded complexes of other aromatics. We also obtained the spectra of intermolecular hydrogen-bonded complexes of the benzoic acid dimer as well as the benzoic acid monomer hydrogen bonded to water and acetic acid. From the monomer complexes, location of  ${}^1(\pi,\pi^*)$  state of the isolated monomer was estimated. Discussions are also made of the electronic states of the dimer and monomer and their relationships to solvent effects on the emission properties.

#### Introduction

The electronic spectra of benzoic acid have been the subject of extensive investigations for a long time. The main reason for the interest comes from the well-known fact that benzoic acid forms a hydrogen-bonded cyclic dimer. The effect of dimerization on the ultraviolet absorption spectrum of benzoic acid was investigated in solution at low temperature by Ito et al.<sup>1</sup> who identified the  $1(\pi,\pi^*)$  states of the monomer and dimer. The emission properties of the monomer and the dimer were examined in rigid glass solution at 77 K by Baba and Kitamura.<sup>2</sup> They found that the monomer shows phosphorescence alone, whereas the dimer emits not only phosphorescence but also fluorescence. The absorption and emission spectra of the benzoic acid dimer in benzene single crystal at 2 K were reported in a series of papers by Baum and McClure.<sup>3,4</sup>

From the above studies, considerable information has been accumulated on the electronic states, the vibronic structure, and

the emission mechanisms in the condensed phase. However, important information on the lowest  $(n,\pi^*)$  state is still missing for both the monomer and the dimer. Since the  $(n,\pi^*)$  state must play an important role in the relaxation processes, its experimental identification is highly desired. Moreover, solvent effects on the  $(n,\pi^*)$  state will be very important in understanding the electronic processes in condensed media. The problems inherent in the electronic state of benzoic acid arise in part from the lack of information on isolated monomer and dimer molecules, having no external perturbation. The electronic spectra of benzoic acid vapor may provide such information. However, the vapor spectra at room temperature are broad (see Figure 1) because of the congestion caused by the presence of many hot bands, and consequently they do not provide useful information. In this regard, recently developed supersonic jet spectroscopy would be very powerful since the spectral congestion is removed by the low temperature attained by supersonic expansion. Very recently, Poeltl and McVey<sup>5</sup> have reported for the first time the fluorescence excitation spectrum of the  $(\pi,\pi^*)$  state of the benzoic acid dimer in a supersonic jet and proved the usefulness of this method. Although the  $(n,\pi^*)$  state of the dimer was not detected, their

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