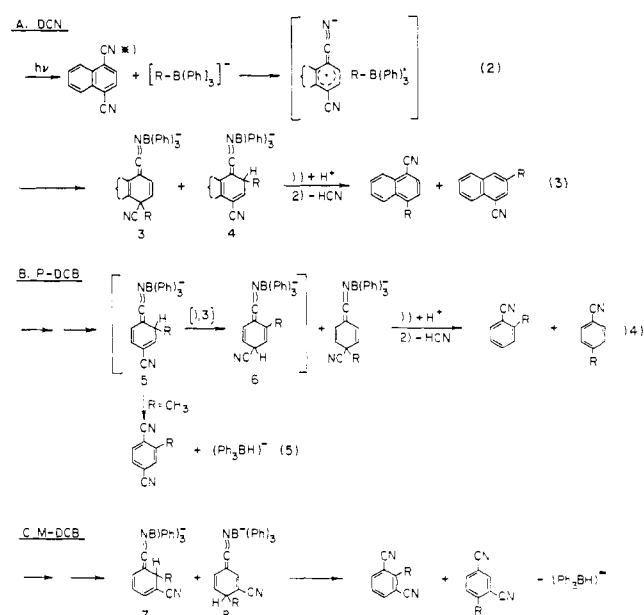


Scheme I



o- and *p*-toluonitrile and 2-methyl-1,4-dicyanobenzene (Table I). In this case, the transferred methyl group has been substituted for either a cyano group or a hydrogen on the original dicyanoarene. The same phenomenon is observed for *m*-DCB, but in this instance formation of alkylidicyanobenzenes accounts by far for the chief products. Similar results are obtained when benzylborate **2** is used.

It is possible from the results described above to formulate a tentative mechanistic rationale. This proposal is outlined in Scheme I. The first steps in the mechanism are common to all of the dicyanoarenes we examined and are illustrated for DCN. Irradiation creates the excited singlet of the arene which is quenched by electron transfer to generate the dicyanoarene radical anion¹⁵ and an alkyltriphenylboron radical. Eventual cleavage^{7,8} of the oxidized borate at the bond between the alkyl carbon and boron releases the alkyl group and triphenylboron. We suggest these components combine with DCN⁻ to form the isomeric ketiminoborates **3** and **4** (eq 3). Protonation and dehydrocyanation complete the reaction sequence and generate the observed products.

The ketiminoborates formed from *p*- and *m*-DCB apparently have alternative reaction paths available. For the former, intermediate **5** may tautomerize to **6** before protonation and dehydrocyanation releases the *o*-alkylbenzonitrile. The ketiminoborates **7** and **8** (in part **5**) must undergo an elimination of perhaps triphenylborohydride or its equivalent to form the isolated alkylated dicyanobenzene products.

The mechanism outlined in Scheme I is but one of several that can account for the observations. Additional experiments are required to define the process more clearly. Nevertheless, the potential utility of the photooxidation of alkyltriphenylborates is clear from our findings. These reagents mediate the efficient transfer of alkyl groups to excited electron acceptors. There is no reason to expect that the acceptors must be restricted to dicyanoarenes. Work is under way to define the scope of this process.

Acknowledgment. We thank Professor Larry Faulkner of this department for the use of cyclic voltammetric equipment and Professor J. C. Martin for a sample of 2,6-dicyanotoluene. We specially thank Professor Scott Denmark for suggesting the synthesis of 3-methyl-1-cyanonaphthalene. This work was supported by a grant from the Mead Corporation and in part by the National Science Foundation.

(15) The negative charge of cyanoaromatic radical ions is thought to be mainly localized on nitrogen: Longster, G. F.; Myatt, J.; Todd, P. F. *J. Chem. Soc. B* 1967, 612.

Registry No. (Me)₄N⁺[MeB(Ph)₃]⁻, 98689-31-7; (Me)₄N⁺[PhCH₂B(Ph)₃]⁻, 98689-33-9; 1,3-NCC₆H₄CN, 626-17-5; 1,4-NCC₆H₄CN, 623-26-7; 2-NCC₆H₄CH₃, 529-19-1; 4-NCC₆H₄CH₃, 104-85-8; 2-NCC₆H₄CH₂Ph, 56153-61-8; 4-NCC₆H₄CH₂Ph, 23450-31-9; 3-NCC₆H₄CH₃, 620-22-4; 1,4-dicyanonaphthalene, 3029-30-9; 3-methyl-1-cyanonaphthalene, 71235-72-8; 4-methyl-1-cyanonaphthalene, 36062-93-8; 3-benzyl-1-cyanonaphthalene, 98689-34-0; 4-benzyl-1-cyanonaphthalene, 78075-59-9; 2-methyl-1,4-dicyanobenzene, 55984-93-5; 2-benzyl-1,3-dicyanobenzene, 98689-35-1; 4-benzyl-1,3-dicyanobenzene, 98689-36-2; 2-methyl-1,3-dicyanobenzene, 2317-22-8; 4-methyl-1,3-dicyanobenzene, 1943-88-0; 4-bromo-1-methylnaphthalene, 6627-78-7.

Adsorption and Reactivity of Acetylene on a Cu(110) Surface

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Received July 1, 1985

Outka et al.¹ recently reported that acetylene on a Cu(110) surface is largely nondissociatively adsorbed and desorbs reversibly in a broad temperature region with peaks at 280, 340, and 375 K. Additionally, it was reported that ~340 K some disproportionation occurred to ethylene, which desorbed molecularly, and an irreversibly adsorbed carbonaceous residue which accounted for 11% of the initially adsorbed acetylene. This disproportionation to release ethylene was cited as the first reported reaction of this kind under ultrahigh vacuum conditions.

In this paper I report relevant aspects of a more extensive high-resolution electron energy loss (EEL) and thermal desorption (TD) spectroscopic study of the adsorption and reactivity of acetylene on (110) and (100) copper surfaces. In particular, this work shows that Outka et al. failed to detect the major desorption product, benzene, and appear to have erroneously attributed mass spectrometric fragments of benzene to ethylene.

Multiplexed TD spectra (2, 26, 27, 78) from a saturated surface indicated that hydrogen (2), acetylene (26), and benzene (78) were desorbed (solid lines, Figure 1). Although a small pulse of *m/e* 27 was seen, this must be attributed to mass spectrometric fragmentation of benzene and not ethylene. The contribution to the *m/e* 27 (and 26) spectra (5.5% of parent 78) from this source are shown by the dashed lines. Reaction-limited hydrogen desorption² (not shown in Figure 1) was seen in a broad region between 600 and 900 K with two poorly defined maxima near 650 and 800 K.

It is apparent from these observations that trimerization to benzene is the main surface process. Trimerization to benzene is a well-known homogeneously catalyzed reaction but only recently has been reported on low-index single-crystal surfaces of palladium³⁻⁵ under ultrahigh vacuum conditions comparable to that used in the present study.

Figure 2 shows EEL spectra recorded after heating saturated monolayers of (a) C₂H₂ and (b) C₂D₂ to ~280 K. Prominent bands are listed and assigned in Table I. The band at 690 cm⁻¹ in the C₂H₂ spectrum is assigned to the γ(CH) mode of coadsorbed benzene from the trimerization reaction. This assignment is in accordance with other work in this laboratory with benzene alone on Cu(110) which showed a similar dominant band near 700 cm⁻¹ and reversible desorption in a broad structureless region between 200 and 310 K. The remaining bands are assigned to nondissociatively adsorbed acetylene. These assignments follow those proposed by Bandy et al.⁶ for C₂H₂ and C₂D₂ on Cu(111), the

(1) Outka, D. A.; Friend, C. M.; Jorgensen, S.; Madix, R. J. *J. Am. Chem. Soc.* 1983, 105, 3468.

(2) Wachs, I. E.; Madix, R. J. *Surf. Sci.* 1979, 84, 375.

(3) Gentle, T. M.; Muettterties, E. L. *J. Phys. Chem.* 1983, 87, 2469.

(4) Sesselmann, W.; Woratschek, B.; Ertl, G.; Kuppers, J.; Haberland, H. *Surf. Sci.* 1983, 130, 245.

(5) Tysoe, W. T.; Nyberg, G. L.; Lambert, R. M. *J. Chem. Soc., Chem. Commun.* 1983, 623.

(6) Bandy, B. J.; Chesters, M. A.; Pemple, M. E.; McDougall, G. S.; Sheppard, N. *Surf. Sci.* 1984, 139, 87.

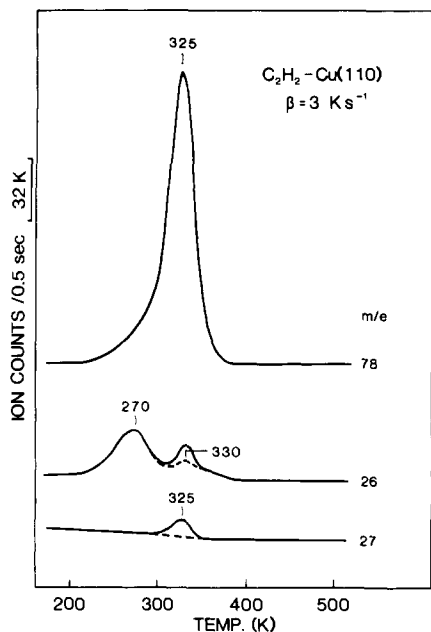


Figure 1. Multiplexed TD spectra following acetylene adsorption on a Cu(110) surface at 90 K. The heating rate was 3 K s⁻¹.

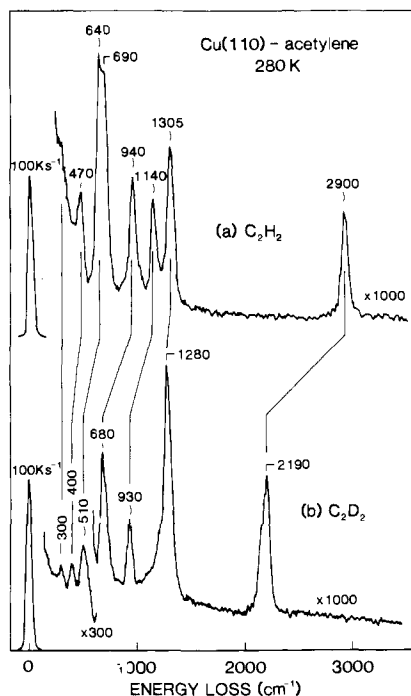


Figure 2. EEL spectra of (a) C₂H₂ and (b) C₂D₂ on Cu(110) obtained after saturating the surface at 100 K and annealing to 280 K.

Table I. Frequencies (cm⁻¹) and Assignments of the EEL Bands from Acetylene Adsorption on Cu(110) at 280 K

assignment	C ₂ H ₂	C ₂ D ₂	H/D
ν(CH)	2900	2190	1.32
ν(CC)	1305	1280	1.02
δ _{as} (CH)	1140	930	1.23
δ _s (CH)	940	680	1.38
γ(CH)	640	510 ^a	1.25
Cu-acetylene modes	470	400	
		300	
γ(CH) benzene	690	510 ^a	

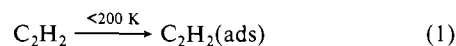
^a Unresolved.

spectra of which are similar to those seen here on the Cu(110) surface except for the activity of the δ_{as}(CH) mode in the present spectra. Similarly, additional work in this laboratory has shown

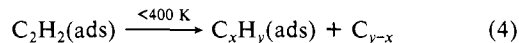
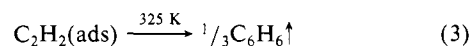
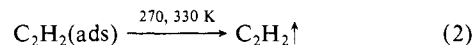
that the Cu(100) surface produced acetylene spectra very similar to those from the Cu(111) surface. The insensitivity of the band near 1300 cm⁻¹ to deuterium substitution leaves little doubt as to its assignment to stretching of the CC bond which must be of ~1.5 order implying strong interaction with the surface. Furthermore, the similarity of the spectra on these low-index copper surfaces suggests a common adsorption site, most probably a two-fold bridge although it does not appear possible to distinguish between a CC bond vector parallel or perpendicular to CuCu axis on the basis of these EEL spectra.

After the sample was heated to 400 K the EEL spectrum reveal weak bands near 770, 870, and 3010 cm⁻¹ (550, 720, ~2250 cm⁻¹ with deuterated acetylene). The 870 (720) cm⁻¹ band was attenuated after heating to 600 K. The remaining two bands survived 700 K but were attenuated after 800 K. These spectra show that reaction-limited hydrogen evolution in this temperature region is associated with the destructive dehydrogenation of at least two new adsorbed hydrocarbon residues which must have been formed concomitantly with acetylene desorption and trimerization.

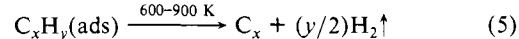
As a result of these observations the adsorption and reaction of acetylene on a Cu(110) surface may be written thus



with three reactions occurring concurrently in the region 200–400 K



followed by



Equation 4 is written in a general form since speculation on the structure and bonding configuration of the species C_xH_y (at least two of them up to 600 K) is beyond the purpose of this paper.

Registry No. C₂H₂, 74-86-2; Cu, 7440-50-8; C₆H₆, 71-43-2.

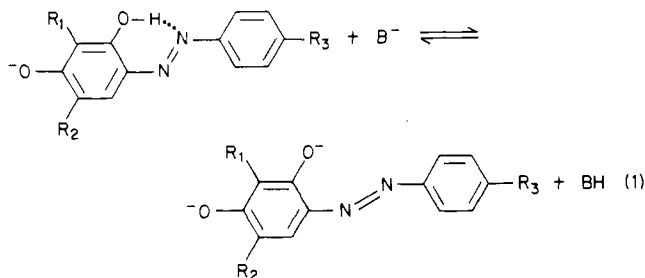
Change in Rate-Limiting Step in Proton Removal from an Intramolecularly Hydrogen-Bonded Acid and the Rate of Opening and Closing of a Hydrogen Bond

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Received May 13, 1985

We wish to report that proton transfer from intramolecularly hydrogen-bonded phenylazoresorcinol monoanions to general bases (B⁻) in 70% (v/v) Me₂SO-H₂O, eq 1, shows a change in rate-



limiting step with base concentration. This has made it possible to obtain values for the rate coefficients and equilibrium constants