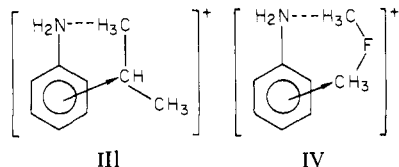


isopropylation of chlorobenzene. The "chelate" is characterized by the electrostatic interaction of the cation with both the π electrons of the substituent and the π system of the ring, e.g.,



Such electrostatic complexes can be conceivably formed by $C_2H_5^+$, $i-C_3H_7^+$, $t-C_4H_9^+$, CH_3CO^+ , and even by $(CH_3)_2F^+$, which is probably characterized by a planar structure similar to that of a carbenium ion.²⁸

While the "chelates" III formed by carbenium ions cannot be distinguished on the grounds of their m/e ratios from the anilinium ions I or the arenium ions II, it is tempting to assign the "chelate" structure IV to the $(M + (CH_3)_2F^+)$ ion actually observed, if with low abundances, in the CH_3F CI spectra of aniline.

The electrostatic "chelate" can evolve into different ionic species, i.e., protonated aniline, the N-substituted ion I, or the arenium ion II, whose relative proportions depend on the nature, the structure, and the charge distribution of the electrophile involved. Thus, the "assisted" ring-substitution mechanism can be expected to contribute little to ortho acetylation, since CH_3CO^+ would tend to bind preferentially to the hard N base of aniline. Consequently, the relatively low proportions of ortho-acetylated isomers from aniline, as well as from phenol and anisole,^{32,34} are likely to reflect

essentially the rate of the *direct* attack on the ortho positions of the ring.

Conclusion

It is customary to close the discussion of any given gas-phase aromatic substitution with a comparison involving the corresponding reaction occurring in solution. Such comparison is difficult in the present case because of the meagerness of data on the reactivity of aniline in substitution processes occurring in solution, whose study is complicated by the basic properties of the amine. In fact, the electrophilic species behaving as Brønsted or Lewis acids interact with the amino group, changing the very nature of the substrate and preventing the kinetic study of the free amine.³⁷ As a consequence, most of the data from solution-chemistry experiments refer to *derivatives* of aniline, such as *N,N*-dimethylaniline or acetanilide, whose reactivity is of course entirely different from that of the free amine.

In conclusion, perhaps is not unwarranted to claim that the results of this gas-phase study provide the first data on the intramolecular selectivity of the electrophilic attack on *free* aniline, irrespective of the reaction environment, at least as far as substitution by electrophilic carbon is concerned.

Acknowledgment. The authors acknowledge the financial support from Italian National Research Council (CNR), the experimental help of C. Sparapani and A. DiMarzio, and the useful discussions with P. Giacomello.

Registry No. C_6H_5Me , 108-88-3; NMe_3 , 75-50-3; $C_2H_5^+$, 14936-94-8; $i-C_3H_7^+$, 19252-53-0; $t-C_4H_9^+$, 14804-25-2; CH_3CO^+ , 15762-07-9; Me_2F^+ , 64710-12-9; CH_4 , 74-82-8; C_3H_8 , 74-98-6; $i-C_4H_{10}$, 75-28-5; CH_3F , 593-53-3; CO , 630-08-0; O_2 , 7782-44-7; aniline, 62-53-3.

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Infrared Laser Induced Heterogeneous Reactions: 2-Propanol with Cupric Oxide

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Abstract: The heterogeneous decomposition of 2-propanol vapor in the presence of CuO solid has been induced by infrared laser radiation. The reaction produces both acetone by dehydrogenation and propene by dehydration. Yields and branching ratios are quite sensitive to experimental variables. Experiments have been carried out in one of two basic configurations: either the CuO surface is parallel to the laser beam as it passes through the cell or the CuO surface is perpendicular to and intercepts the laser beam. Reaction occurs in both geometries although much more readily in the latter. Branching ratios from 0.02 to 6.0 have been observed.

Introduction

Infrared multiphoton absorption by polyatomic molecules to induce chemical reactions has been demonstrated to be a fairly general phenomenon.¹ In a typical experiment, a gas-phase sample at relatively low pressure is placed in the beam path of an infrared laser and excited to some high vibrational level of the electronic ground state. If sufficient energy has been deposited in the sample, chemical reaction can occur. It is possible to exert some control over the reactivity of the sample by controlling

irradiation variables. Choices for these parameters, like laser power or frequency, in turn control which components of a complex mixture absorb radiation and the number of photons they absorb.² Nevertheless, the resulting homogeneous decomposition usually leads to products predominantly via the lowest energy reaction pathway of the absorbing species.³

In principle, the chemical versatility of this activation method could be substantially enhanced through the use of heterogeneous gas/solid reaction channels.⁴⁻⁶ This added variable, a catalytic

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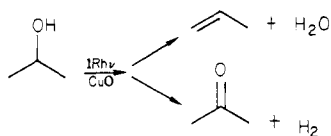
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Scheme I



material, would allow one to control not only the energy distribution in the reacting ensemble through laser variables, but also the potential energy surface over which reactions occur through the appropriate choice of a catalytic substance. We wish to report experiments designed to probe the utility of IR multiphoton activation as a means of initiating heterogeneous chemistry at gas/solid interfaces. The system we have chosen to examine is the oxidation of 2-propanol to acetone and propylene over cupric oxide. Thermal activation of this heterogeneous reaction has been examined,⁷ and it has found some industrial use.⁸ In this paper we demonstrate that considerable control over the product ratios can be obtained by changing and/or combining variations of the following parameters: CuO quantity, orientation of the CuO surface relative to the incident beam, laser fluence, and frequency.

Experimental Section

2-Propanol, certified ACS Spectranalyzed grade (99.9%), was obtained from Fisher Scientific Co. It was stored in a gas bulb, and used after several freeze-thaw cycles. CuO was prepared by direct oxidation of Cu metal. Sheet metal was sanded with silicon carbide paper until visibly shiny. Samples were checked for impurity levels by X-ray photoelectron spectroscopy X-ray (PES). In general, oxygen was the chief impurity at ~16% levels. The polished metal was formed into ~1-cm² plates or hexagonal prisms with faces ~1 cm in width. The polished metal forms were oxidized in a quartz pyrolysis tube for 18 min by heating the samples from room temperature to 300 °C under an O₂ flow of ~2 L/min.⁹ The resulting samples were black green in color, indicative of CuO. X-Ray PES analysis showed CuO with little or no Cu₂O.¹⁰

The excitation source was a grating tuned Lumonics TEA 101 CO₂ laser operated at 0.5 Hz. The beam was focused with a 15-in. focal length ZnSe lens. Qualitatively reproducible beam profiles were obtained by checking the beam quality with thermal sensitive paper. Frequencies were determined with an Optical Engineering 16A CO₂ spectrum analyzer. The power was monitored by a Scientech 362 power-energy meter. Fluences were determined from the measured laser power and the cross-sectional area of the beam at a surface. The cross-sectional area was determined from the measured diameter of the burn pattern on thermal paper. The reaction vessel was a 250-mL round-bottom flask, modified with the appropriate gas inlet ports and fitted with laser quality NaCl windows. The catalyst was mounted on a rotatable stopcock at the center of the cell so that it could be moved in and out of the laser beam (for CuO flats) or turned to expose new faces (for CuO hexagons). The cell was filled to a known pressure of material from 40 to 500 mtorr on a vacuum line equipped with a Baratron 227 capacitance manometer. Reactions were carried out by mounting the cell within the laser beam path. Conditions which were varied included laser frequency, power, gas pressure, catalyst geometry relative to the beam, and the number of pulses. The reaction mixture was analyzed by GC (Varian 2400 fitted with a gas injection port, interfaced with a Hewlett-Packard 3390A integrator) utilizing either a 10% Carbowax 1540 on Chromosorb W column for separation of the hydrocarbons from acetone and 2-propanol or a 10% β,β' on Chromosorb W column to separate the hydrocarbons from one another. Identification of the major components was established by GC coinjection, gas-phase FTIR (Digilabs FTS-20) and GC-MS (Finigan 4000C1).

Results and Discussion

We have observed two different reaction channels in these experiments as shown in Scheme I. The presence of acetone and

Table I.^a Effect of Catalyst/Beam Geometry on Product Ratio

reaction geometry	yield (%)	branching ratio ^d
1. no CuO	44 ± 5	43.0
2. CuO laser parallel ^b	51 ± 6	14.0
3. CuO laser perpendicular ^c	80 ± 7	7.4

^a All experiments at 40 mtorr 2-propanol, 1070.5 cm⁻¹, 0.54 ± 0.05 J/pulse, 500 pulses. The laser is focused to a fluence of ~8 J/cm² at the focal point. ^b Focal point centered 5 mm above surface. ^c Surface blocks beam at focal point. ^d [hydrocarbon]/[acetone].

Table II.^a Effect of Catalyst Position on Product Ratio

CuO surface position ^b	yield (%)	branching ratio ^c
1. +8	15 ± 2	0.8
2. +5	38 ± 4	3.8
3. +3	63 ± 6	6.1
4. 0	80 ± 7	7.4
5. -5	81 ± 7	7.2

^a All experiments at 40 mtorr 2-propanol, 1070.5 cm⁻¹, 0.54 ± 0.05 J/pulse, 500 pulses. The laser is focused to a fluence of ~8 J/cm² at the focal point. ^b In cm relative to the focal point at 0, where the CuO position in entries 1-3 is in front of the focal point and entry 5 is behind it. ^c [hydrocarbon]/[acetone].

propene in the product mixtures has been established by gas chromatography coinjections, and by FTIR and GC-MS analysis of the product mixture. In general, the mass balance by gas chromatography is adequate and no other significant reaction channels are implied. However, while acetone is stable under the reaction conditions, propene is not, and significant secondary chemistry of propene can occur under certain conditions. The secondary chemistry requires CuO and leads mainly to propane. Propane formation apparently employs hydrogen liberated from the alcohol in the oxidation to acetone. H₂ and H₂O are not analyzed by these flame ionization gas-chromatography-based techniques.

Both total yield and branching ratio ([hydrocarbon]/[acetone]) are very sensitive to experimental parameters. Experiments have been carried out in two basic configurations; either the CuO surface is parallel to the laser beam as it passes through the cell or the CuO surface is perpendicular to and intercepts the beam. The results of experiments using a focused laser beam and these two reaction geometries are shown in Table I. In all cases an 2-propanol pressure of 40 mtorr and a frequency of 1070.5 cm⁻¹, P(08) 001-020, where 2-propanol is a fairly strong absorber was employed. Irradiation was carried out using 500 pulses with 0.54 ± 0.05 J delivered per pulse. The beam area at the focal point is approximately 10% that of the collimated beam, and in the parallel experiment the focal point is located ~5 mm above the CuO surface. The first entry of Table I shows that in the absence of CuO under focused conditions there is substantial laser-induced reaction of 2-propanol. This homogeneous reaction gives almost entirely propene. Addition of a cupric oxide surface in either of the two geometries has significant effects. The effect on both yield and branching ratio is more pronounced in the perpendicular geometry (entry 3) where the CuO surface intercepts the laser beam. Even in the parallel experiment, however, where the laser does not interact directly with the surface, enhancement of the dehydrogenation channel is evident.

Within the perpendicular geometry, significant control over yields and branching ratios is possible simply by changing the position of the surface relative to the focal point. The data are shown in Table II. As the surface is moved from in front of the focal point to beyond the focal point, the total product yield increases, and the product mixture becomes progressively richer in hydrocarbon. It is interesting that the data taken 5 cm beyond the focal point is roughly equivalent to the sum of the uncatalyzed experiment (entry 1, Table I) and the catalyst 5 cm in front of the focal-point (entry 2, Table II) experiment. The trends in the

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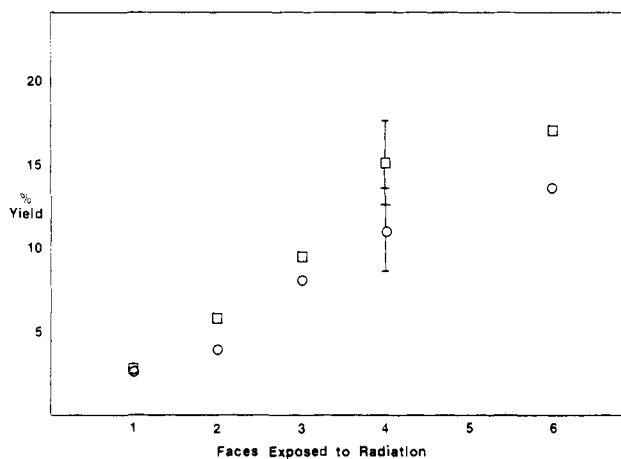


Figure 1. Yields of acetone O, and hydrocarbon (propane + propene), □ as a function of number of CuO surfaces exposed to laser (100 mtorr 2-propanol, 600 pulses, 0.60 J/pulse, perpendicular geometry, +8 cm, 1037.4 cm⁻¹).

data can be rationalized, at least qualitatively, by an increasing proportion of homogeneous reaction, unimolecular dehydration to propene, as the vapor is exposed to progressively increasing energy densities. An apparently homogeneous IR-laser-induced dehydration of 2-propanol has been previously observed.¹¹

With the surface 8 cm in front of the focal point (entry 1, Table II), reaction is essentially the exclusive result of heterogeneous effects. This conclusion can be drawn from the following experiments. When pure 2-propanol at 40 mtorr is irradiated with a telescoped laser beam at a fluence of 1.03 ± 0.05 J/cm², only $4.9 \pm 0.8\%$ decomposition occurs over 500 pulses. Under these conditions, the beam is collimated and is not significantly attenuated (<5%) as it passes through the cell. Thus there exists a cylindrical volume of alcohol vapor uniformly exposed to the laser. In the heterogeneous experiment of entry 1, Table II, the CuO surface intercepts the beam halfway through the cell. The beam fluence through the irradiated volume never exceeds 1 J/cm², which is the fluence of the pure 2-propanol experiment. But, the volume of vapor exposed to the laser is approximately only half as large. Therefore, a maximum homogeneous yield of $2.5 \pm 0.8\%$ would be expected for entry 1. The data show that sixfold higher yields are obtained. Furthermore, branching ratios rich in acetone relative to the homogeneous conditions are observed. The conditions of entry 1, Table II, where it is clear that the chemical outcome is dominated by the heterogeneous reaction channel, are used to generate the remaining data (Figures 1 and 2, and Table III).

The nature of the solid surface has an important influence on the chemical outcome. If the beam is stopped with a nonoxidized copper surface, the extent of decomposition is small, roughly what one would expect from the homogeneous component alone. Furthermore, the catalytic activity of the oxidized surface depends strongly on the number of pulses delivered. This is demonstrated in Figures 1 and 2. In these two experiments "CuO hexagons" were employed. The data in Figure 1 show acetone yields and hydrocarbon yields where 600 pulses were divided evenly among some subset of the six available faces. Thus one face represents 600 pulses at a single surface, two faces 300 pulses at each of two, etc. Clearly exposure of new CuO to the beam during photolysis enhances the yield. Both reaction channels increase roughly in direct proportion to the number of faces exposed to the laser. The data further imply that the effect of a single surface is exhausted in fewer than 100 pulses. This point is amplified by an experiment in which the number of pulses per face was varied between 5 and 100. The data show virtually all chemistry occurs within the first five pulses delivered to a given CuO surface. During the course of reaction, it appears as though CuO is blown off the irradiated region exposing the bare metal subsurface. This in itself probably

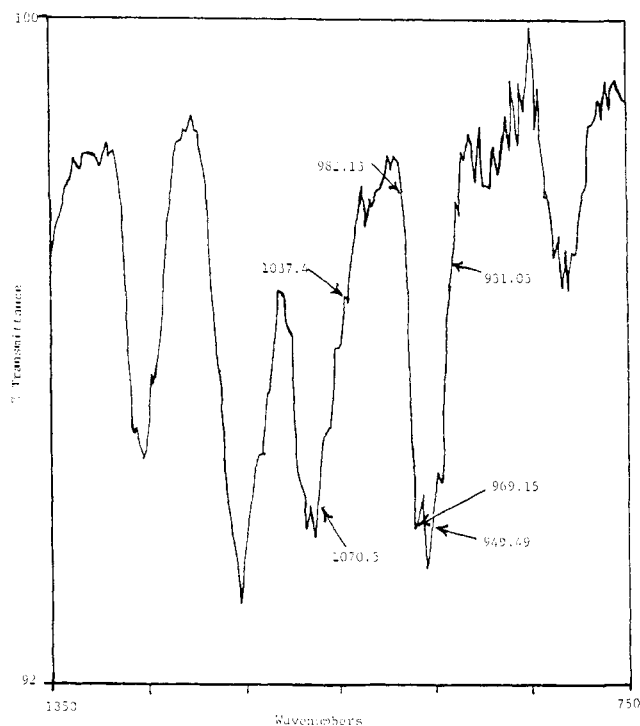


Figure 2. Gas-phase 2-propanol spectrum (~ 2 torr) in the region of IR laser (900–1100 cm⁻¹) with frequencies used in experiments on the spectrum.

Table III

frequency	without CuO ^b yield (%)	with CuO ^a	
		yield acetone	yield hydrocarbon (%)
931.05	24 ± 2	4.8 ± 0.5	2.8 ± 0.1
949.49	12 ± 1	1.8 ± 0.1	0.5 ± 0.1
969.15	9 ± 1	1.4 ± 0.6	0.7 ± 0.3
982.13	5 ± 1	3.9 ± 0.1	0.8 ± 0.2
1037.43	9 ± 1	4.1 ± 0.3	0.8 ± 0.2
1070.46	40 ± 4	3.0 ± 0.4	1.6 ± 0.4

^a CuO experiments at 100 mtorr 2-propanol, fluence ~ 0.86 J/cm² at the surface, surface perpendicular to the laser beam at +8 cm, 500 pulses. ^b Total product yield (%) 130 mtorr 2-propanol ~ 5.4 J/cm² at the focus, no CuO.

accounts for the loss of catalytic activity.¹² X-ray PES confirms a substantially diminished oxygen content on the postphotolysis surface. The oxygen to copper ratio on a photolyzed catalyst was roughly equivalent to a preoxidized clean Cu surface.

Yields and branching ratios also show some dependence on irradiation frequency. This is illustrated in Table III, where yields for each pathway in the heterogeneous experiment as well as relative multiphoton decomposition yields from uncatalyzed 2-propanol are listed. This heterogeneous experiment employed the perpendicular geometry at 100 mtorr of alcohol and a common fluence of 0.86 J/cm² at the surface. Some reaction occurs at all frequencies. Although the differences are not large, it is interesting that the higher hydrocarbon yields are obtained at the same frequencies where multiphoton absorption in the alcohol vapor, as indicated by the yields of the uncatalyzed reaction, is maximized (931, 1070 cm⁻¹). Acetone yields are also frequency dependent, but, except for the high yield at 931.05 cm⁻¹, show no obvious correlation to either the gas-phase absorption spectrum of 2-propanol (Figure 2) or to the multiphoton decomposition yield in the pure vapor (Table III).

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Although at this point we have very little mechanistic insight into the CO₂-laser-induced heterogeneous chemistry of 2-propanol on CuO, it is apparent that controlled chemistry can be carried out this way. We have made no effort to maximize the yield of one reaction channel and are still in the process of investigating systematic variations in pressure, catalyst composition, and fluence. Nevertheless, even over this fairly limited investigation of the phenomenon, branching ratios ranging from 0.02 to 6 have been observed. At a minimum, our data require both homogeneous and heterogeneous pathways to products. The homogeneous reaction yields largely hydrocarbon, while the heterogeneous pathway gives principally acetone. Much of the tunability in the branching ratio appears to result from changes in the proportions of reaction from these two pathways that can be induced by altering reaction conditions. It would be very difficult to obtain comparable tunability in the branching ratio using normal thermal activation. Pyrolysis of alcohols in the presence of metal oxides usually leads preferentially to dehydrogenation.¹³ In the specific system we have employed, 2-propanol with CuO, quantitative data

for both reaction channels have apparently not been reported, but it is clear that at relatively low temperatures (~200 °C) acetone is by far the principal product.^{7,13} At higher temperatures hydrocarbon products become more prominent, but a range of at least several hundred degrees Centigrade would be required to duplicate the full range of branching ratios observed in the laser chemistry.¹⁴ Pyrolysis of the alcohol in the absence of metal oxides appears to give surface-initiated free-radical chemistry leading mainly to acetone.¹⁵ The estimated barrier for the homogeneous dehydration reaction is 67 kcal/mol, approximately 12 kcal/mol higher than the radical pathway for pyrolysis.¹⁵

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Polymeric Surfactant Vesicles. Synthesis and Characterization by Nuclear Magnetic Resonance Spectroscopy and Dynamic Laser Light Scattering

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Abstract: [CH₃(CH₂)₁₅][CH₂=CH(CH₂)₈CONH(CH₂)₆][CH₃]₂N⁺Br⁻ (1), [CH₃(CH₂)₁₄CO₂(CH₂)₂][CH₃][CH₂CH=CH₂]⁺N⁺Br⁻ (2), [CH₃(CH₂)₁₄CO₂(CH₂)₂]₂NCOCH=CHCO₂H (3), and [CH₃(CH₂)₁₇]₂NCOCH=CHCO₂H (4) have been synthesized. Sonication of these surfactants led to the formation of vesicles. Vesicles could be polymerized by exposure to ultraviolet radiation or by the use of azoisobutyronitrile (AIBN) as an initiator. Vesicles prepared from 1 polymerized in their bilayers. Vesicles prepared from 2, 3, and 4 have double bonds on their headgroups and could, therefore, potentially polymerize both at the inner and outer surfaces or separately at either surface. Polymerization of vesicles prepared from 2, 3, and 4 by ultraviolet radiation resulted in the closing of both surfaces. Conversely, addition of AIBN to a solution of these vesicles and subsequent incubation at 80° led to the selective "zipping-up" of the outer surface only. Following the loss of vinyl protons of the surfactant vesicles by ¹H NMR spectroscopy provided evidence for polymerization. Presence of vesicles has been demonstrated by substrate entrapment, gel filtration, and dynamic laser light scattering. Increasing the sonication time led to smaller and less polydisperse vesicles. On polymerization, vesicles maintained the sizes of their nonpolymeric counterparts. Polymeric vesicles were found to be appreciably more stable than their unpolymerized analogues. Polymeric vesicles retained the fluidities of vesicles and underwent thermotropic phase transitions. Addition of KCl led to the growth of both unpolymerized and polymeric surfactant vesicles.

Completely synthetic surfactant vesicles provide useful media for the development of chemistry based on membrane-mediated processes.⁵ Areas investigated in membrane mimetic chemistry include reactivity control,⁵⁻⁷ recognition,⁸ solar energy conversion,⁹

drug delivery,¹⁰ and analytical applications.¹¹ These studies have been considerably aided by the large surface potentials and charge

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