(t, CH_2-OPh), 80.39 and 81.45 (2 d, C-2, C-6, or reversed), 86.57 (s, C-8), 114.9, 120.94, 129.55 (3 d, Ph), 159.56 (s, Ph).

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Supplementary Material Available: Tables of positional parameters, bond distances, bond angles, and general displacement parameter expressions (*U*'s) of **5** and experimental procedures for the preparation of **7a**, **7c**, **4**, and **5** (4 pages). Ordering information is given on any current masthead page.

Neutron Spectroscopic Evidence for Adsorbed Hydroxyl Species on Platinum Black

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In recent years, there has been growing vibrational spectroscopic evidence for the existence of stable OH species adsorbed on single-crystal metal surfaces using electron energy loss spectroscopy (EELS). In particular, EEL spectra of OH species have been documented on Pt(111),[1] Pd(100),[2-4] Ag(110),[5] Ni(110),[6,7] and Rh(100)[8] surfaces. In contrast, there has been a scarcity of studies confirming the stability of OH species on high-surface-area metallic materials using other appropriate vibrational spectroscopic techniques. Morrow and Ramamurthy,[9] in one infrared (IR) study of some silica-supported group VIII metals, observed bands in the OH stretching region (430–460 meV) after the reaction of O_2 with hydrogen-covered Pt, Ir, Rh, Ni, Co, and Fe as well as after the reaction of H_2O with a partially reduced PtO surface.

In this paper, incoherent inelastic neutron scattering (IINS) was used to provide vibrational spectroscopic evidence for the formation of stable OH species adsorbed on an unsupported, microcrystalline, metal powder surface, namely, Pt black, in direct comparison with the reported EEL spectrum for OH/Pt(111).[1] The neutron's high sensitivity to vibrations involving hydrogen motions renders IINS a particularly useful technique for characterizing the vibrational spectra of hydrogenous adsorbates on high-surface-area materials.[10] Moreover, many IR-opaque materials, such as Pt black, are essentially neutron-transparent.

The Pt sample was prepared similar to previously described procedures.[11] Platinum black[12] (150 g) was washed in concentrated nitric acid at 295 K to remove residual potassium to less than 1 ppm (as measured by atomic absorption), rinsed in distilled water, loaded into a gold-sealed aluminum cell, and vacuum-dried at 373 K for 24 h. Surface oxygen was removed by saturating the sample with hydrogen[12] at 143 K, evacuating at 383 K for 24 h, reducing further in flowing H_2 at 383 K for 72 h, and finally evacuating at 383 K for >72 h. Hydrogen was initially introduced at such a low temperature to inhibit any particle sintering (i.e., surface-area reduction) due to localized heating from the exothermic formation of H_2O. The reduced sample (12-nm average crystallite size with 17 $m^2\ g^{-1}$ BET surface area) prepared in this fashion has been shown to possess approximately 0.4 monolayers of residual adsorbed hydrogen as evidenced by both deuterium isotope exchange and IINS intensity measurements.[11,13]

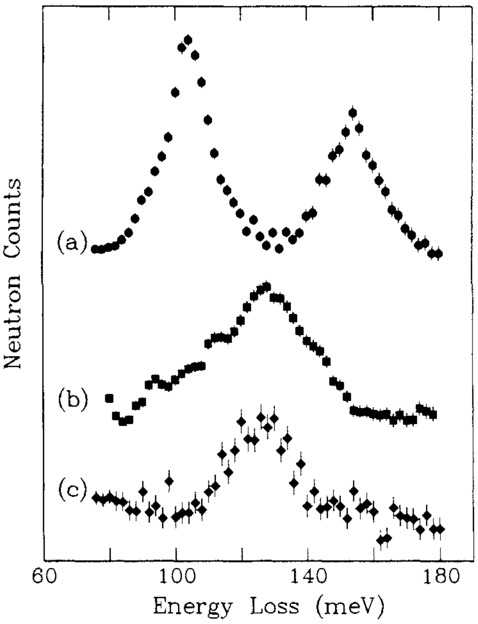

Figure 1. The IINS spectra (a) of residual hydrogen on Pt black, (b) after oxygen-titration of the residual hydrogen, and (c) after the addition of H_2 and O_2 to the oxygen-titrated surface (difference spectrum). See text for details. All spectra have been normalized to the same linear intensity scale.

In an attempt to produce stable surface OH species, the residual hydrogen on the Pt black was titrated with O_2[12] (O:H $\approx$ 1) at 80 K, and the sample was annealed to 300 K over several hours and then recooled to 80 K. The 300 K annealment step was performed to ensure the homogeneous equilibration of H_2O and surface oxygen reaction products throughout the sample. The reported OH/Pt(111) results[1] have indicated that the 80 K recooling step should lead to the formation of stable surface OH species via the back reaction of the H_2O and surface oxygen. After spectral analysis, the oxygen-titrated Pt black surface was further dosed with H_2 at 80 K followed by an equivalent dose of O_2, enough to make an additional 0.5 monolayer of OH species. The sample was again annealed to 300 K over several hours and then recooled to 80 K for spectral analysis.

The IINS measurements were made at the National Bureau of Standards Research Reactor on the BT-4 Be-filter spectrometer with 40-min collimation before and after the Cu(220) monochromator. Energy resolution was a function of the incident energy: ca. 5–6 meV (1 meV = 8.065 cm^{-1}) below 90 meV and ca. 6% of the incident energy above 90 meV. All spectra were measured at 80 K and were corrected for fast-neutron background contributions where appropriate.

The IINS spectra are illustrated in Figure 1. The vibrational spectrum of the residual hydrogen on Pt black following the sample cleaning procedure, Figure 1a, indicates two scattering peaks maximized at 104 and 152 meV.[13] The assignment of these hydrogen modes is left for discussion in a subsequent paper.[14] The vibrational spectrum following the titration of the residual hydrogen with O_2, Figure 1b, indicates that the hydrogen scattering features have been replaced, for the most part, by a single band

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(12) Platinum black was obtained from Engelhard. Hydrogen and oxygen (Research Grade) were obtained from Spectra Gases. Manufacturers are identified in order to provide a complete description of experimental conditions. This is not intended as an endorsement by the National Bureau of Standards.

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peaked at 128 meV. The vibrational spectrum due to the addition of both H_2 and O_2 to the oxygen-titrated surface is illustrated in Figure 1c by the difference spectrum, i.e., the H_2/O_2-dosed surface minus the O_2-titrated surface spectrum. Similar to Figure 1b, the reaction of the H_2 and O_2 on the Pt surface yields additional scattering intensity peaked at 128 meV. The position of this spectral feature is in excellent agreement with the EELS value of 128 meV reported for the δ_{M-OH} (i.e., bending) mode of OH on Pt(111) by Fisher and Sexton.[1] Extension of the IINS spectra above 200 meV yielded no additional scattering intensity at the expected position of the H-O-H scissor mode at 202 meV for adsorbed H_2O on Pt[1,15] suggesting that the Pt black surfaces represented by Figure 1 (parts b and c) do not possess any significant amount of adsorbed H_2O species. Hence, based on the comparison with the reported EELS results, the neutron scattering feature at 128 meV is assigned to the Pt-O-H bending mode of adsorbed OH species present as the dominant hydrogenous species on the Pt black surface for O:H ratios of unity.

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The Generation of 1,4-Biradicals in Rigid Media: Crystal Structure–Solid State Reactivity Correlations

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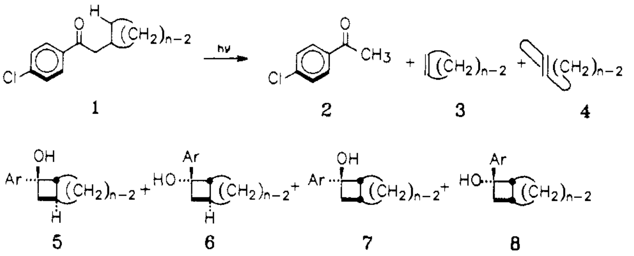
It is now well established that the crystalline phase provides a reaction medium in which reactants, intermediates, and final products have an enforced geometrical similarity, thereby enabling the development of detailed crystal structure–reactivity relationships.[1] In this communication we report an investigation of the type II photochemistry of the homologous ketones **1a–e** (Scheme I), both in the solid state and in solution. The photochemical results, along with the crystal and molecular structures of all five ketones, provide the basis for an increased general understanding of the reactivity of the intermediate 1,4-hydroxybiradicals in terms of structure.

Ketones **1a–e** were prepared by Friedel–Crafts acylation of chlorobenzene by using the appropriate acid chloride.[2] Each ketone was photolyzed (nitrogen laser, 337 nm) at 0 °C in its crystalline state as well as in a 0.1 M benzene solution at room temperature; conversions were kept low (<5% in the solid state; <20% in solution). Visual inspection of irradiated single crystals revealed retention of crystallinity with uniform reaction throughout, and the product ratios were not sensitive to attempts to increase surface area or introduce defect sites by, e.g., grinding. Table I summarizes the general finding that, as the cycloalkyl group is varied from cyclobutyl to cyclooctyl, there is a dramatic (if irregular) decrease in the extent of Norrish type II cleavage and a corresponding increase in the amount of cyclobutanol formation.

Scheme I



(**a**) n = 4, (**b**) n = 5, (**c**) n = 6, (**d**) n = 7, (**e**) n = 8

Table I. Photoproduct Ratios and Crystallographic Data for α-Cycloalkyl-*p*-chloroacetophenones

			% cleavage		dihedral angles[b]	
ketone	mp (°C)	R[c]	crystal	benzene (Φ)[d]	ϕ_1[e] (deg)	ϕ_4[f] (deg)
1a (*n* = 4)	50–51	0.035	92	90 (0.20)	+90	−45
1b (*n* = 5)	60–61	0.061	92	92 (0.29)	+90	−65
1c (*n* = 6)	63–64	0.053	40	39 (0.35)	+85	−88
1d (*n* = 7)	42–43	0.042	61	55 (0.25)	+85	−100
1e (*n* = 8)	48–49	0.039	18	25 (0.16)	+84	−135

[a] Determined by quantitative GC analysis of the amount of *p*-chloroacetophenone produced; the % cyclization is given by (100 − % cleavage). [b] Defined with reference to structure **10**, Scheme **II**. The mirror image of **10**, which is present in equal amounts (racemic space groups), has the signs of ϕ_1 and ϕ_4 reversed. [c] Crystallographic discrepancy factor (R factor). [d] Solution quantum yields were determined at 313 nm in a merry-go-round apparatus by using valerophenone as the actinometer. [e] Dihedral angle between top lope of p-orbital at C(1) and C(2)–C(3) bond. [f] Dihedral angle between the top lobe of the hypothetical p-orbital at C(4) (assumed to lie perpendicular to the C-(3)–C(4)–C(5) plane) and the C(2)–C(3) bond.

Separation difficulties and low yields prevented isolation of the cyclobutanol photoproducts from ketones **1a** and **1b**, but cyclobutanols **5c–e**, **6c–e**, **7c**, and **8c** could be isolated and their structures assigned. The assignments rest on the X-ray crystal structures of cyclobutanols **5c** and **5e**, which clearly show the trans ring junction stereochemistry. With these compounds as reference points, the remaining structural assignments were made by using 400 MHz ^1H NMR spectroscopy.[2] This revealed that the trans-fused cyclobutanols **5** and **6** are the major photoproducts from ketones **1c–e**; GC peaks attributable to the cis-fused cyclobutanols **7** and **8** constitute less than 20% of the total cyclobutanols in each case, both in the solid state and solution.[3] For ketone **1c**, the **5c**:**6c**:**7c**:**8c** ratios are 24:31:3:3 (benzene) and 23:30:4:3 (crystal). For the other four cyclobutanols that were characterized, the ratios are **5d**:**6d** = 6:34 (benzene), 7:29 (crystal) and **5e**:**6e** = 12:49 (benzene), 12:65 (crystal).

Another key aspect of photoproduct structure concerns the geometry of the cycloalkenes formed by cleavage. By using authentic samples of *cis*- and *trans*-cyclooctene for comparison purposes,[4] capillary GC analysis of the reaction mixture from photolysis of ketone **1e** revealed that both isomers are formed. The cis:trans ratios (extrapolated to 0% conversion owing to isomerization under the reaction conditions) were 90:10 (benzene) and 72:28 (crystal). Experiments designed to provide evidence for the formation of *trans*-cycloheptene by trapping with acidic methanol[5] were unsuccessful; no attempts were made to detect *trans*-cycloalkenes from photolysis of ketones **1a–c**.

A mainstay of the interpretation of solution phase 1,4-biradical reactivity over the years has been the idea that, in order for efficient cleavage to occur, the radical-containing p-orbitals should be parallel to the carbon–carbon bond undergoing scission (0,0 geometry).[6] It seems likely that cyclization, which requires

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(1) For two recent review articles on organic photochemistry in the solid state, see: (a) Scheffer, J. R.; Garcia-Garibay, M.; Nalamasu, O. In *Organic Photochemistry*; Padwa, A., Ed.; Marcel Dekker: New York, 1987; Vol. 8, Chapter 4. (b) Ramamurthy, V.; Venkatesan, K. *Chem. Rev.* **1987**, *87*, 433.

(2) Details of the characterization of all reactants and photoproducts will be presented in a full paper.

(3) In an earlier communication on portions of this work (Ariel, S.; Ramamurthy, V.; Scheffer, J. R.; Trotter, J. *J. Am. Chem. Soc.* **1983**, *105*, 6959), the two major cyclobutanols from ketone **1c** were mistakenly assumed to have the cis ring junction stereochemistry.

(4) *trans*-Cyclooctene was prepared by the method of Inoue et al. (Inoue, Y.; Takamuku, S.; Kunitomi, Y.; Sakurai, H. *J. Chem. Soc., Perkin Trans. II* **1980**, 1672).

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