Contribution from the Department of Chemistry, University of North Dakota, Grand Forks, North Dakota 58202

Highly Efficient Electron-Transfer Processes over Thermally Activated Alkaline Earth Oxides. Monolayer Anion Radical Formation with Nitrobenzene–MgO and High Concentrations of CO Radicals over MgO, CaO, SrO, BaO, and ThO_2

K. J. Klabunde,* R. A. Kaba, and R. Morris

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For more than 10 years it has been known that thermally activated MgO allows facile electron-transfer processes to occur on its surface. Tench and Nelson[1] studied the interaction of nitrobenzene with thermally activated MgO[2] at room temperature and the facile formation of $C_6H_5NO_2^-\cdot$. From their powder EPR studies they concluded that this anion radical laid flat on the MgO surface and was able to rotate parallel to the surface about the nitrogen. They attributed the ready formation of the anion radical to the presence of coordination defects on the MgO surface. In similar work Lunsford and Jayne[3] studied the facile formation of CO radicals on thermally activated MgO. They formulated the CO radical as slightly positively charged and in a strongly synergistic donor–acceptor surface bonding mode similar to classical M–CO bonds in transition-metal complexes. Lunsford and Jayne attributed the CO surface radical formation to the presence of transition-metal impurities on the MgO surface, in particular iron impurities. Brey and coworkers[4] and Meriadeau and co-workers[5] have carried out similar studies on CO–ThO_2 interactions and have proposed the formation of an interesting series of CO-derived surface radical species.[4]

Due to our interest in CO reduction processes as well as the use of CO–H_2O as a reducing medium over basic metal oxide catalysts,[6] we have examined in greater detail some of the MgO electron-transfer work. In particular we have been interested in elucidating in a quantitative way whether electron-transfer processes are of major importance on the surface and what types of sites are involved.

Are these electron processes due to very minor impurities and/or defects on the MgO surface, or are they important in a stoichiometric sense? That is, how many surface MgO molecules per radical are needed? Employing a double-resonator system on a Bruker ER 420/10V EPR spectrometer, we measured the absolute number of spins for the $C_6H_5NO_2^-\cdot$/MgO system. The MgO was "99.99%" purity (ROC/RIC) and was washed with distilled water, dried, powdered, and heat treated in vacuo at 600 °C overnight.[7] The surface area of this MgO was determined with good precision by BET methods[8] as 140 m^2/g. Employing simple volume and area calculations where 8.86 Å^2 was taken as the surface needed for one MgO molecule, it can be determined that the total MgO/surface MgO molecules ratio is 9.4. A sample of the activated MgO was treated with nitrobenzene which caused the color to change from white to yellow and then brown. Radical growth was allowed to proceed for about 1 week, at which time a brown color remained. Spectra were recorded frequently during this period and after, and it was determined that a maximum radical concentration was reached in 1–2 days at 25 °C. Absolute spin counts at the maximum radical concentration, employing DPPH/KCl as standard in the double-cavity apparatus, yielded a value of 6.7×10^{19} $C_6H_5NO_2^-\cdot$ spins/g of MgO. This value was reproducible within 20%. *It indicates that approximately 20–25 surface MgO molecules are necessary for the formation of one anion radical.* Thus, this electron-transfer process is extremely important on the surface even in a stoichiometric sense. In addition, if the $C_6H_5NO_2^-\cdot$ species is considered to be laying flat on the surface and rotating on the N axis, it can be estimated that approximately 18 MgO molecules would be swept out in a steric sense. That is, *our results indicate that essentially a monolayer of $C_6H_5NO_2^-\cdot$ species is formed on MgO.*[9]

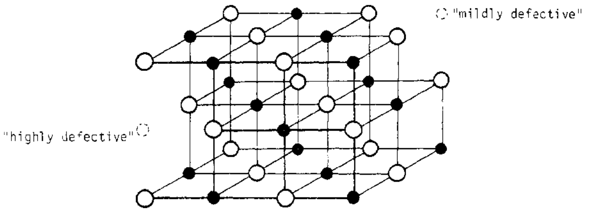

Figure 1. Possible representation of microcrystalline defects in MgO crystallites. The dark small circles represent Mg^{2+} while the larger circles represent O^{2-}. The dashed circles represent areas where Mg^{2+} ions are missing.

Similar studies were carried out on the CO–MgO system. We defer until later publications speculation as to the bonding and nature of the radical and at this time will simply refer to the species formed as CO·. Exposure of white thermally activated (600 °C) MgO to CO at 25 °C caused the formation of a peach color which darkened to a dark orange with time. Maximum radical concentration was attained in 30–60 days. Absolute spin counts yield a value of 1.5×10^{18} spins/g of MgO which is reproducible within 20%. This indicates a ratio of 1000 surface MgO/CO· formed, which definitely indicates that CO· formation is a much more selective process than $C_6H_5NO_2^-\cdot$ formation. Furthermore, quantitative studies on the amounts of CO adsorbed on the MgO at 25 °C yield $(9.9 \pm 3.2) \times 10^{18}$ molecules of CO/g of MgO. *Therefore, about 15% of the CO adsorbed eventually formed radical species.*

We conclude from these studies that these radical-forming processes are extremely important and not due to artifacts or minor impurities. We have in fact measured the amount of Fe impurity in the MgO employed and found ca. 18 ppm, which, even with surface concentration effects, could not account for the large number of CO radicals formed and most assuredly not the number of $C_6H_5NO_2^-\cdot$ species formed. Moreover, since we can detect no free electron centers (F or S centers) in the white thermally activated MgO, we conclude that Tench and Nelson[1] are correct in their interpretation that coordination defects on the MgO surface are responsible. To clarify what this may mean, Figure 1 has been included. A clean MgO surface would have natural defects at corners and steps much in the same way metal surfaces do.[10] On MgO, high electron density sites could be present at these defects due to the absence of a Mg^{2+} ion.[11] The resultant "left over" O^{2-} anions would be coordination defects where molecules of reasonable high electron affinity could pull electrons. The extent of this coordination defectiveness (the number of O^{2-} in the vicinity of the Mg^{2+} ion deficiency) would determine the overall activity of the site. Perhaps only the "most defective" sites interact with CO, but for $C_6H_5NO_2$ even mildly defective sites must interact. It should be noted at this point that prior addition of the Lewis acid CO_2 completely inhibits the production of radicals with either CO or $C_6H_5NO_2$, providing strong evidence that electron-rich sites are indeed responsible for the radical processes. Naturally, the sites described in Figure 1 are only two types of defects of the many that may be present and only serve to illustrate possible modes of interaction with molecules of reasonably high electron affinity.

We have tested a large number of other metal oxides for activity in the CO process and have determined that MgO, CaO, SrO, BaO, and ThO_2 all possess activity. Soon we will report in detail on these studies, and in particular on surface

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requirements, on differences with variation in thermal activation temperatures, and on what other types of molecules interact.

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Registry No. MgO, 1309-48-4; CaO, 1305-78-8; SrO, 1314-11-0; BaO, 1304-28-5; ThO_2, 1314-20-1; $C_6H_5NO_2^{-}\cdot$, 15753-78-3; CO·, 630-08-0.

References and Notes

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(7) Future publications will describe variations in MgO activity with pretreatment temperatures: 500 °C yields one of the most active MgO samples.

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Contribution from the IBM Research Laboratory,
San Jose, California 95193

Reactions of Tetrasulfur Tetranitride with Liquid Bromine and Iodine Monochloride

G. Wolmershäuser and G. B. Street*

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The reactions of tetrasulfur tetranitride with halogens have been the subject of numerous investigations.[1-3] Though the fluorination[4] and chlorination[5] are well understood, leading to such products as NSF, NSF_3, or $(NSF)_4$ and NSCl or $(NSCl)_3$, respectively, the bromination does not proceed analogously and has been reported to give a variety of products including $S_4N_4Br_6$[1] and $(NSBr)_x$.[2,3] Recently the reaction of sulfur–nitrogen compounds with bromine and also iodine monochloride has become a topic of renewed interest because of their influence on the electrical properties of $(SN)_x$ and their ability to cause spontaneous polymerization of S_4N_4.[6,7] Bromine increases the conductivity[8] of $(SN)_x$ by an order of magnitude and also increases the superconducting transition temperature by ~25%[9] whereas ICl only doubles the conductivity. Long exposure of $(SN)_x$ to ICl leads to decomposition and shorter exposure leads only to surface reaction. Electron diffraction[10] and Raman studies[11] indicate the presence of ICl. In contrast it has been shown from Raman[11,12] and far-IR studies[13] that brominated $(SN)_x$ contains the tribromide ion Br_3^-. The influence of the resulting charge transfer on the band structure of $(SN)_x$ has been invoked to explain the increase in the normal-state conductivity as well as the superconducting transition temperature.[14] Both Br_2 and ICl vapors also react with S_4N_4 to give conducting solids.[6,7,15] In the case of bromine vapor the reaction with solid S_4N_4 leads to spontaneous polymerization to $(SNBr_{0.4})_x$, identical with the product of bromination of $(SN)_x$. ICl vapor and solid S_4N_4 lead to a more complicated reaction. Although compositions such as $(SN(ICl)_{0.4})_x$ have been isolated, the iodine–chlorine ratio is usually less than unity. Previously Clever and Muthmann[1] reported that bromine vapor reacted with solid S_4N_4 to give garnet red crystals of $S_4N_4Br_6$. We have observed that if S_4N_4 was brominated with liquid bromine instead of bromine vapor, the major product was an insulating yellow solid. A similar compound was formed upon reaction of S_4N_4 with liquid ICl. Motivated by these anomalies, we have investigated the reaction of S_4N_4 with Br_2 and ICl, under a variety of conditions. In this note we report on the reaction of S_4N_4 with liquid bromine and iodine monochloride.

Table I.

Observed Infrared Frequencies (cm^{-1})			
$S_4N_3Br_3$ in Br_2 Solution	Solid $S_4N_3Br_3$ (Nujol)	Solid $S_4N_3ICl_2$ (Nujol)	Solid S_4N_3Cl[13] (Nujol)
1185,vs	1165,vs	1176,s	1163,s
1145,m	1125,m		1125,w
			1102,vw
1030,vs	1010,vs	1017,vs	998,vs
970,vw			
942,vw	940,vw	902,vw	
		849,w	
742,w	722,w	720,w	
680,vs	675,s	675,s	678,s
	632,w		
618,m	605,w		606,w
572,s	575,w		
560,s	565,s	566,m	561,s
	535,m		
472,s	475,vs	477,vs	466,s
430,m	435,m	440,w	451,s
341,m	320,s	322,s	317,m

Experimental Section

General Procedures. S_4N_4 was prepared according to the literature[16] and fractionally sublimed before use. All solvents and bromine were dried and distilled and the reactions were carried out in the absence of moisture, either under vacuum or in a dry nitrogen or argon atmosphere. The IR spectra were recorded in NaCl, KBr, and polyethylene cells using a Perkin-Elmer IR grating spectrophotometer, Model 283. Differential thermal analysis (DTA) and thermogravimetric analysis (TGA) were carried out using glass, platinum, or gold sample containers. Elemental analysis was performed by the University of California, Analytical Services, Berkeley, Calif.

Preparation of $S_4N_3Br_3$. S_4N_4, 456 mg (2.47 mmol), was heated with 0.8 mL of bromine at ~70 °C in a sealed evacuated glass tube. After 2 days the tube (which now contained a pressure of gas even at liquid nitrogen temperatures due to the liberation of N_2) was carefully opened, and the excess bromine was removed by pumping for at least 4 h at room temperature, leaving an orange-yellow solid—$S_4N_3Br_3$(I). In order to obtain crystals of I the bromine must be removed very slowly (several days) until no bromine atmosphere develops over a period of 2 h after the pumping is interrupted. The yield of I was 1020 mg (100%). Anal. Calcd for $S_4N_3Br_3$: Br, 58.47; N, 10.25; S, 31.27. Found: Br, 58.8; N, 10.3; S, 30.5.

Determination of Liberated Nitrogen. S_4N_4, 368 mg (2 mmol), and 1 mL of bromine were placed in a flask connected via a reflux condenser to a gas buret. All joints were lubricated with halogen-resistant grease. After 24 h of refluxing, the nitrogen evolved was measured to be 22.7 mL at STP or 0.5 mol/mol of S_4N_4.

Preparation of $S_4N_3ICl_2$. S_4N_4, 500 mg (2.71 mmol), was heated with 1.5 mL of ICl at ~100 °C for 48 h in the same experimental setup used for $S_4N_3Br_3$. After the tube was opened the excess ICl and the I_2 which was also formed were removed by pumping for 24 h at ~50 °C. The yield of yellow-orange polycrystalline material

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