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Formation of Paramagnetic Adsorbed Molecules on Thermally Activated Magnesium and Calcium Oxides. Further Studies of Carbon Monoxide

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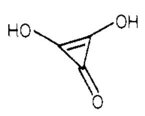
Abstract: Adsorption of CO onto thermally activated MgO or CaO leads to the formation of a variety of adsorbed anionic species. Included is the $C_6O_6^{2-}$ species (rhodizonate), which can be converted to $C_5O_5^{2-}$ (croconate) by heating or by treatment with a variety of adsorbing secondary chemical reagents. The $C_5O_5^{2-}$ species is also favored when lower thermal activation temperatures (400–500 °C rather than 600–1000 °C) for the MgO and CaO are used. Paramagnetic anionic species also form during CO adsorption, and extensive ESR studies with computer simulations and chemical studies have indicated that the major radical anion is cyclic $C_6O_6^{3-}\cdot$. This rhodizonate trianion is adsorbed on the surface in such a way that only two carbons (using ^{13}CO) strongly interact magnetically with the unpaired spin density. Upon treatment of the adsorbed $C_6O_6^{3-}\cdot$ with heat, H_2, HCl, H_2O, CO_2, or NH_3, other adsorbed conformers were identified on the basis of ESR studies. The trianion is inert at 25 °C to N_2, C_2H_4, $C_6H_5CH_3$, and CH_4 and, in fact, can be prepared in the presence of $C_6H_5CH_3$.

The reduction of CO over surfaces or in homogeneous solution is a fascinating topic, which has attracted a great deal of interest for many years.[1] Direct reductions using alkali metals have been very successful. For example, reduction of CO with potassium metal leads to telomerized anionic CO species such as $(K_3C_2O_2)_x$ and $(KCO)_x$ and upon heating to 170 °C leads to cyclic $K_6C_6O_6$.[2-4] With sodium metal at 280–340 °C, $Na_6C_6O_6$ can be prepared.[5] However, at lower temperatures dimeric species such as $M^+O^-C{=}C{-}O^-M^+$ have been prepared.[6-8] In fact, under low-temperature matrix isolation conditions, the codeposition of CO and Li leads to $Li^+CO^-\cdot$, $Li^+C_2O_2^-\cdot$, and $Li^+C_2O_2^{2-}Li^+$.[9] And lastly, electrochemical reduction of CO is also possible and has led to the production of the cyclic squarate dianion, $C_4O_4^{2-}$.[10,11]

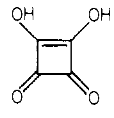
Several of these reduced CO telomers are well-known and have been under investigation for some time. The three-, four-, five-, and six-membered ring species are all known.[12-14]

deltic acid



1

squaric acid



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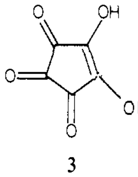
croconic acid



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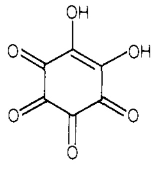
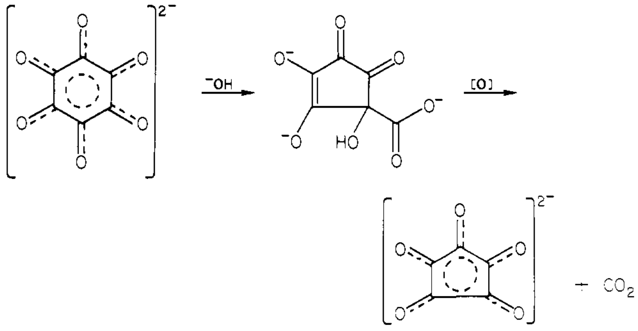
rhodizonic acid



4

Rhodizonic acid (**4**) is quite unstable under basic conditions, and oxidative ring contraction to croconic acid (**3**) takes place readily. It is proposed that the dianion $C_6O_6^{2-}$ is an intermediate in this ring contraction.[5]



West and co-workers[5,15,16] have spectroscopically analyzed several of these oxocarbon dianion species and believe that the dianions of **3** and **4** exist as planar, electron-delocalized (aromatic) structures. However, Aihara[17] presents evidence that only the dianion of **1** has much resonance stabilization energy and that the dianions of **3** and **4** are lacking in this respect.

Electrochemical oxidation of $C_4O_4^{2-}$, $C_5O_5^{2-}$, and $C_6O_6^{2-}$ has been performed in each case successfully, yielding $C_4O_4^-\cdot$, $C_5O_5^-\cdot$, and $C_6O_6^-\cdot$ in solution. The isotropic ESR g values were determined to be 2.005 84, 2.006 24, and 2.006 52, respectively.[18] Only the croconate monoanion showed ^{13}C hyperfine splitting ($A_{^{13}C}$ = 4.1 G). The rhodizonate dianion could be reduced to the paramagnetic trianion. An ESR g value of 2.00 57 was recorded. No hyperfine splitting was observed.[18] Attempts to further reduce the squarate and croconate dianions were apparently unsuccessful.

Considering catalytic and surface reduction schemes for CO, only in rare cases have species been trapped or isolated that appear to be intermediates. Some of the metal formyl complexes recently prepared may be relatives of important intermediates in Fischer–Tropsch and related chemistry, but it is very difficult to be certain.[1] In this context, it is interesting that some basic metal oxide surfaces are ideal for generating and trapping CO in reduced forms.[19-29] Several investigators have been interested in the

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(1) (a) G. W. Parshall, "Homogeneous Catalysis", Wiley-Interscience, New York, 1980, p 77; (b) J. M. Thomas and W. J. Thomas, "Introduction to the Principles of Heterogeneous Catalysis", Academic Press, New York, 1967, p 401.

(2) P. J. Chantry, *Phys. Rev.*, **172**, 125 (1968).

(3) W. F. Sager, A. Fatiadi, P. C. Parks, D. G. white, and T. P. Perros, *J. Inorg. Nucl. Chem.*, **25**, 187 (1963).

(4) V. A. Shusshunov, *Zh. Fiz. Khim.*, **23**, 1322 (1949).

(5) R. West and J. Niuin "Nonbenzenoid Aromatics", J. P. Snyder, Ed., Academic Press, New York, 1969, p 314.

(6) E. Weiss and W. Buchner, *Helv. Chim. Acta*, **46**, 1121 (1963).

(7) E. Weiss and W. Buchner, *Z. Anorg. Allg. Chem.*, **330**, 251 (1964).

(8) W. Buchner, *Helv. Chim. Acta*, **46**, 2111 (1964).

(9) H. Krishnan Ph.D. Dissertation, Rice University, 1975.

(10) G. Bockmair and H. P. Fritz, *Z. Naturforsch., B*, **30B**, 330 (1975).

(11) G. Silvestri, S. Gambino, G. Filardo, M. Guinazzi, and R. Evcoli, *Gazz. Chim. Ital.*, **102**, 818 (1972).

(12) D. Eggerding and R. West, *J. Am. Chem. Soc.*, **98**, 3641 (1976).

(13) F. Arcamone, C. Prevost, and P. Souchay, *Bull. Soc. Chim. Fr.*, **891** (1953).

(14) W. Stadeli, R. Hollenstein, and W. Philipsborn, *Helv. Chim. Acta*, **60**, 948 (1977).

(15) R. West, H. Y. Niu, D. L. Powell, and M. V. Evens, *J. Am. Chem. Soc.*, **82**, 6204 (1960).

(16) R. West and H. Y. Niu, *J. Am. Chem. Soc.*, **84**, 1324 (1962).

(17) J. I. Aihara, *J. Am. Chem. Soc.*, **103**, 1633 (1981).

(18) E. V. Patton and R. West, *J. Phys. Chem.*, **77**, 2652 (1973).

(19) J. H. Lunsford and J. P. Jayne, *J. Chem. Phys.*, 44, 1492 (1966).

(20) V. Indovina, D. Cordischi, and M. Occhiuzzi, *J. Chem. Soc., Faraday Trans. 1*, **77**, 811 (1981).

(21) D. Cordischi, V. Indovina, and M. Occhiuzzi, *J. Chem. Soc., Faraday Trans. 1*, **76**, 1147 (1980).

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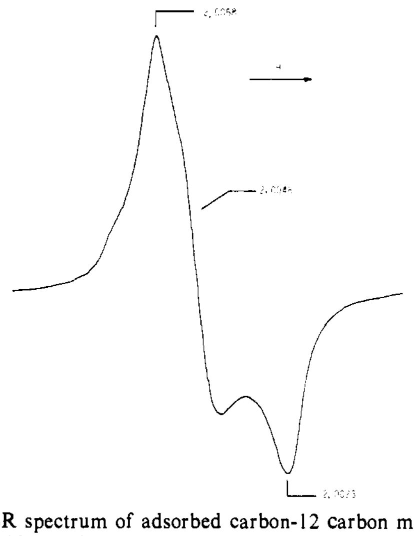

Figure 1. ESR spectrum of adsorbed carbon-12 carbon monoxide on magnesium oxide previously pretreated at 800 °C.

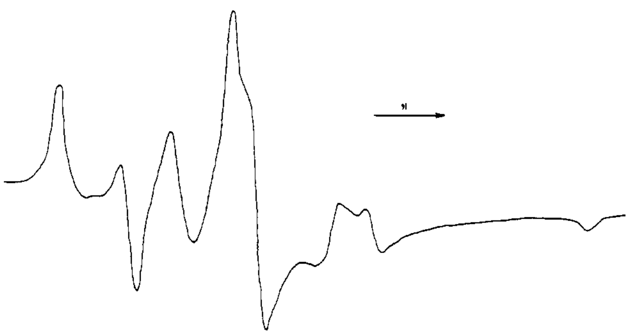

Figure 2. ESR spectrum of adsorbed carbon-13 carbon monoxide on magnesium oxide previously heated at 800 °C.

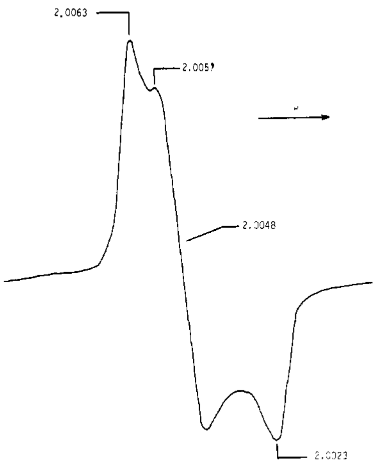

Figure 3. ESR spectrum of adsorbed carbon-12 carbon monoxide on calcium oxide previously pretreated at 800 °C.

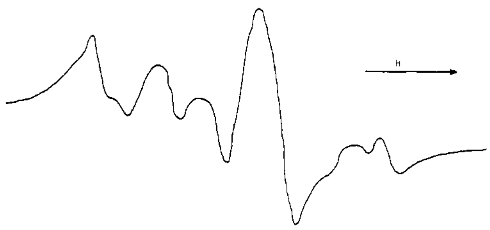

Figure 4. ESR spectrum of adsorbed carbon-13 carbon monoxide on calcium oxide previously pretreated at 800 °C.

CO–MgO,[19–29] CO–CaO,[28,29] and CO–ThO$_2$[30,31] systems for many years. We have recently presented short reviews of this area.[28,29] Basically, Zecchina,[22–27] Stone,[25–27] Cordischi,[20,21] and we[28,29] have concluded that CO adsorbed on thermally activated MgO leads to the production of a variety of homologized $(CO)_x{}^{y-}$ anions as well as $(CO)_2{}^{-}\cdot$. Of particular interest is the report that cyclic $C_4O_4{}^{2-}$, $C_5O_5{}^{2-}$, and/or $C_6O_6{}^{2-}$ are present on the MgO surface.[27]

In this paper we present further investigations regarding the CO anionic radical telomers on MgO and CaO. Earlier, we presented evidence that these species may play a role in Ni-catalyzed reduction of CO to CH$_4$ over MgO.[32,33]

Results and Discussion

Carbon Monoxide Radical Anion Formation. Since the original work of Lunsford and Jayne,[19] Cordischi and co-workers[20,21] and we[28,29] have been involved in studies of the properties and assignment of structure to the radical species formed. Although Cordischi and co-workers worked with MgO–CoO solutions, we believe that the radical anion species formed in all cases (Lunsford, Cordischi, and ourselves) are identical, and slight spectral differences are due mainly to ESR instrumental and inherent sample problems.

For comparison purposes the ESR spectra for $^{12}CO/MgO$, $^{12}CO/CaO$, $^{13}CO/MgO$, and $^{13}CO/CaO$ are presented in Figures 1–4. The g values for the radical anion on MgO are $g_1 = 2.0058$, $g_2 = 2.0048$, and $g_3 = 2.0023$ and on CaO are $g_1 = 2.0063$, $g_2 = 2.0048$, and $g_3 = 2.0023$ with a shoulder at 2.0057. The center lines (largest line) of the ^{13}CO spectra correlate well with the g values observed for ^{12}CO. The general shape and the existence of a center line in the ^{13}CO spectra dictate that the unpaired electron interacts with an even number of equivalent ^{13}C nuclei. The spectrum was assigned as a triplet complicated by the anisotropy of the system.[28] Independently, Cordischi and co-workers came to the same conclusion in their $^{13}CO/MgO–CoO$ work,[21] and direct spectral comparisons confirm this. Looking back, it is not surprising that Lunsford and Jayne[19] were unable to draw these conclusions since their ^{13}CO experiments were difficult to interpret, owing to the presence of a great deal of ^{12}CO in their ^{13}CO sample.

Recall that in order for radical anion formation to occur the MgO must be out gassed at 400–1000 °C at $<10^{-4}$ torr.[28] After cooling of the evacuated samples to 25 °C and addition of CO, the white MgO turned yellow-orange (500 °C pretreatment) or light red (600–1000 °C pretreatment). Similarly, it was necessary to outgass CaO at 600–1000 °C. Upon addition of CO a yellow color developed immediately. Radical anion growth occurred slowly, however.

The CO anion radicals formed on MgO and CaO were indefinitely stable at room temperature is vacuo or under a CO atmosphere. The MgO-supported species could also be stored under N$_2$ (it could even be prepared under N$_2$), but was very sensitive to O$_2$ and H$_2$O. The CaO-supported species was also sensitive to O$_2$, but was not destroyed immediately. Upon O$_2$ exposure the ESR spectrum changed but the yellow color and the new ESR signal persisted for 24–48 h.

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(22) A. Zecchina and F. S. Stone, *J. Chem. Soc., Faraday Trans. 1*, **74**, 2278 (1978).

(23) E. Gugglielminotti, S. Coluccia, E. Garrone, L. Cerruti, and A. Zecchina, *J. Am. Chem. Soc., Faraday Trans. 1*, **75**, 98 (1979).

(24) S. Coluccia, E. Garrone, E. Guggielminotte, and A. Zecchina, *J. Chem. Soc., Faraday Trans. 1*, 77, 1063 (1981).

(25) F. S. Stone and A. Zecchina, *Proc. Int. Congr. Catal., 6th*, 162 (1976).

(26) A. Zecchina, M. G. Lofthouse, and F. S. Stone, *J. Chem. Soc., Faraday Trans. 1*, **71**, 1476 (1975).

(27) A. Zecchina and F. S. Stone, *J. Chem. Soc., Chem. Commun.*, 582 (1974).

(28) R. M. Morris, R. A. Kaba, T. G. Groshens, K. J. Klabunde, R. J. Baltisberger, N. F. Woolsey, and V. I. Stenberg, *J. Am. Chem. Soc.*, **102**, 3419 (1980).

(29) K. J. Klabunde, R. A Kaba, and R. M. Morris, *Adv., Chem. Ser.*, No. **173**, 140 (1979).

(30) W. S. Brey, Jr., R. B. Gammage, and Y. P. Virmani, *J. Phys. Chem.* **75**, 895 (1971).

(31) B. Claudel, F. Juillet, Y. Trambouze, and J. Veron, *Proc. Int. Congr. Catal., 3rd*, **1**, 214 (1965).

(32) K. Matsuo and K. J. Klabunde, *J. Org. Chem.*, 47, 843 (1982).

(33) K. Matsuo and K. J. Klabunde, *J. Catal.*, **73**, 216 (1982).

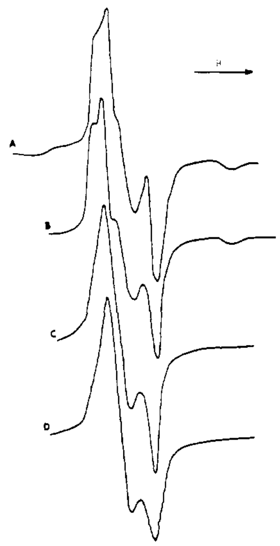


Figure 5. ESR spectra of carbon-12 carbon monoxide adsorbed on magnesium oxide previously pretreated at (A) 400 °C, (B) 500 °C, (C) 600 °C, (D) 700 °C.

Figure 6. ESR spectrum of carbon-13 carbon monoxide adsorbed on magnesium oxide previously heat treated at 500 °C.

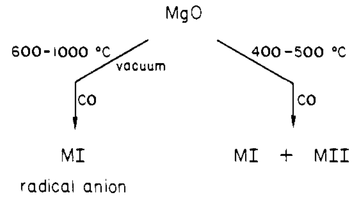
The thermal stability of the MgO-supported species is surprising. Upon careful heating in vacuo, temperatures as high as 225 °C could be reached without ESR spectral changes. At 275 °C the spectrum persisted for 20 min while at 350 °C only for 3 min. However, in a CO atmosphere (150 torr) the radical anion species on MgO was stable up to 450 °C.

These thermal studies also showed that the light red color of the CO/MgO sample is not directly related to the radical species. Thus, at 225 °C, where the radical will persist for reasonable periods, the red color will not, and a bright-yellow color developed.

Even though the color cannot be directly correlated with radical presence, the color is very important in the radical formation. Thus, a variety of reagents that inhibit radical formation also inhibit the color development (CO_2, CS_2, H_2O, H_2S, HCl, NH_3, HC≡CH, CH_3OH, CH_3CH_2OH, CH_3I, CH_3COOH, CH_3COCH_3, $C_6H_5NH_2$). Likewise, under all conditions where color developed, radical anion species also developed, but at a much slower rate. In general color development was almost immediate, whereas radical anion formation took many hours, indeed weeks (at 25 °C), to reach a maximum concentration.

Reaction Studies and Types of Radical Anion Species. The ESR study of CO adsorbed on MgO and CaO is complicated by the presence of more than one radical anion species, the existence of which is obvious from a comparison of a series of CO/MgO spectra on MgO outgassed at 400, 500, 600, and 700 °C. These spectra are shown in Figure 5. At outgassing temperatures of 600 °C or above, the ESR signal shown in Figure 1 is dominant. However, lower outgassing temperatures gave rise to spectra that appeared to be composites of two or more radical types. First, let us examine the effect of O_2 exposure.

As previously mentioned, rapid exposure of the CO/MgO system to O_2 caused destruction of the radical anion and the light red color. However, very gradual O_2 exposure caused a color change from red to yellow and the generation of a new radical whose spectrum was very similar to those obtained from 400 or 500 °C outgassed MgO samples. So it is apparent that the initial radical formed on high-temperature outgassed (600 °C or higher) MgO is very oxygen sensitive but with very gradual O_2 exposure can be converted to another radical that is not oxygen sensitive, which is the same radical formed on low-temperature (400 or 500 °C) outgassed MgO (both radicals are present on the lower temperature outgassed MgO). Experiments with ^{13}CO strongly supported this rationale. Figure 6 shows the spectra obtained with 500 °C outgassed ^{13}CO/MgO. Notice the vast difference as opposed to 800 °C ^{13}CO/MgO (Figure 2). Figure 7 shows the 800 °C outgassed ^{13}CO/MgO after exposure to oxygen and after oxygen-heating treatment. There are indeed strong simularities between the spectra, especially after short heat treatment at 150 °C, which greatly improved resolution. In conclusion, the radical species formed on 400 or 500 °C outgassed MgO are of two types: first the radical anion formed on 800 °C outgassed MgO and second a radical that is similar or identical with that formed by treatment of the first radical anion species with oxygen (very gradually). These radicals are labeled MI and MII.



In the case of CO/CaO the spectra obtained on 600 and 1000 °C outgassed CaO were different in subtle ways, but were clearly not as strikingly different as in the MgO cases described above. Figure 8 illustrates the ^{13}CO/CaO spectra with 600 °C CaO, 1000 °C CaO, and after O_2 treatment. The 600 °C outgassed sample

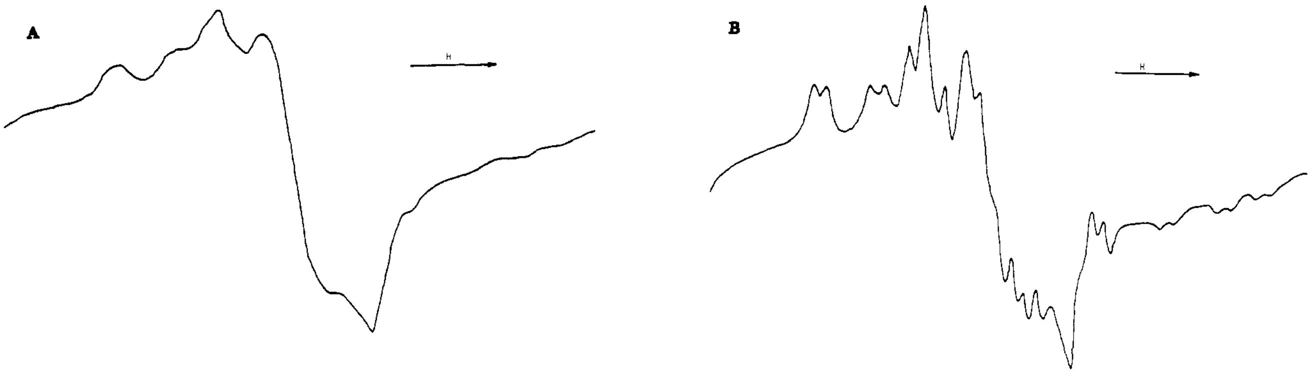


Figure 7. (A) ESR spectrum of carbon-13 carbon monoxide adsorbed on 800 °C outgassed magnesium oxide after exposure to 150-torr oxygen and heated to 150 °C. (B) ESR spectrum of carbon-13 carbon monoxide adsorbed on 800 °C outgassed magnesium oxide followed by exposure to 150-torr oxygen gas.

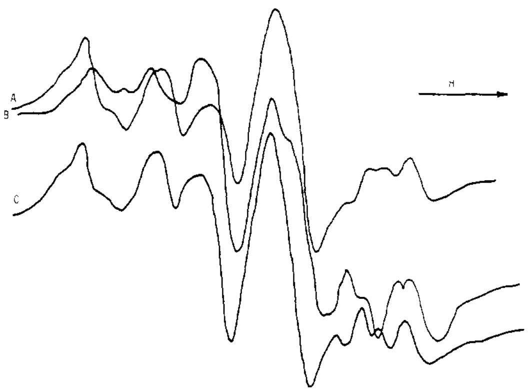


Figure 8. ESR spectra of carbon-13 carbon monoxide on calcium oxide previously outgassed at (A) 1000 °C, (B) 600 °C, and (C) 1000 °C plus exposure to 10-mtorr oxygen.

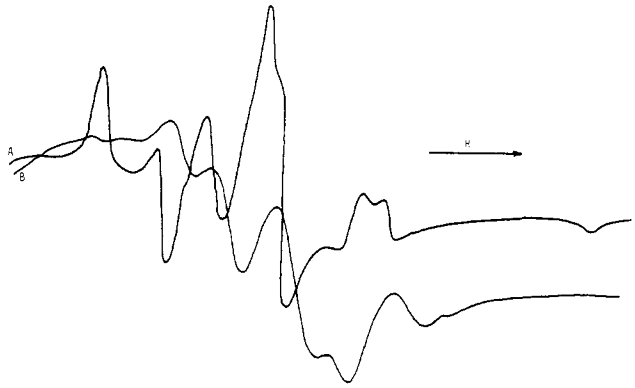


Figure 9. ESR spectra of carbon-13 carbon monoxide adsorbed on 800 °C outgassed magnesium oxide (A) initially and (B) after exposure to 300-torr carbon dioxide.

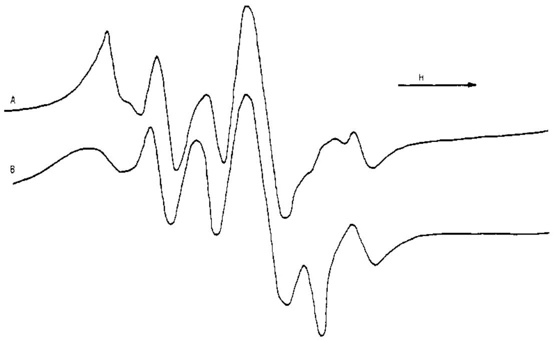


Figure 10. ESR spectra of carbon-13 carbon dioxide on 800 °C outgassed calcium oxide (A) initially and (B) after exposure to 300-torr carbon dioxide.

appeared to be more sensitive to O_2, but in general the CaO radical species was much less sensitive to O_2 treatment than the MgO system.

Changes were also observed when CO/MgO and CO/CaO samples were exposed to CO_2 and H_2O. The spectral changes were often fairly subtle, and there is no evidence that these reagents directly attack the radical anion species. Instead, they may simply perturb the radical anions surface orientation. Figures 9–13 illustrate the CO/MgO and CO/CaO spectra followed by exposure to CO_2 and H_2O. Note that treatment of $^{13}CO/MgO$ (800 °C) with CO_2 or with H_2O led to the same spectrum, and no center line was observed, indicating that one or more of the magnetically active nuclei are no longer involved. This would again suggest that direct reaction did not take place (bond making or breaking) but that CO_2 or H_2O adsorbed on the MgO near the radical anion and forced it to change its orientation and/or electronic distribution.

The effect of HCl addition to CO/MgO was to perturb the system in the same way as CO_2 and H_2O did. Finally, the addition of NH_3 caused some destruction of the paramagnetic species in question, and the remaining (protected?) radical was perturbed as with CO_2 or H_2O.

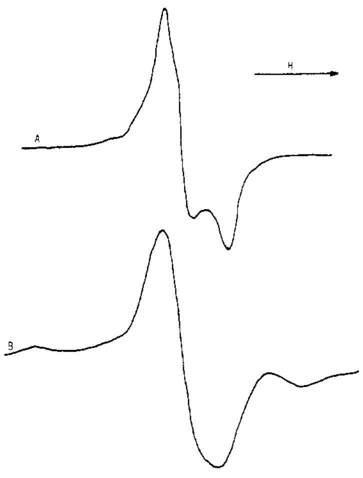


Figure 11. ESR spectra of carbon-12 carbon monoxide on 800 °C outgassed magnesium oxide (A) initially and (B) after exposure to 25-torr degassed water.

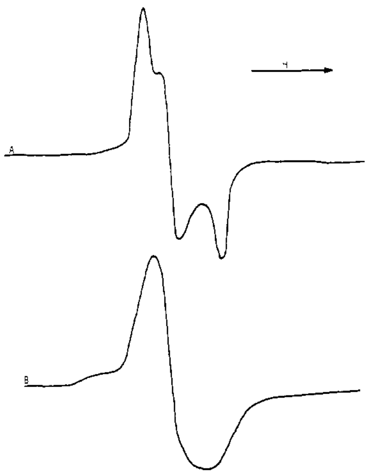


Figure 12. ESR spectra of carbon-12 carbon monoxide on 800 °C outgassed calcium oxide (A) initially and (B) after exposure to 25-torr water.

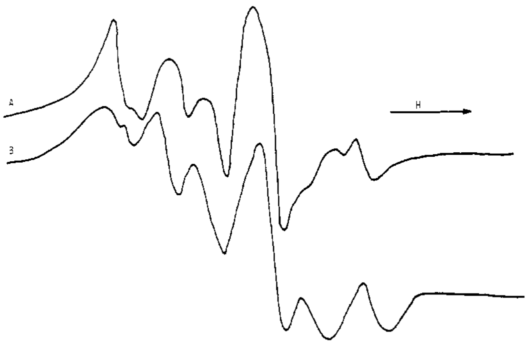


Figure 13. ESR spectra of carbon-13 carbon monoxide on 800 °C outgassed calcium oxide (A) initially and (B) after exposure to 24-torr water.

In summary, reagents that do change the observed spectra do so in a minimal way. Similar *g* values are observed with no evidence of additional hyperfine splitting. Since the spectra are so similar, we conclude that there is not direct attack, but simply conformational perturbation of the radical anion species.

A broad investigation of a series of less polar molecules showed that the CO radical anion species on MgO and CaO were inert toward these species. There was no change in the ESR spectrum upon addition of H_2, $CH_2{=}CH_2$, $CH_3CH{=}CH_2$, $CH_3(CH_2)_2C$-

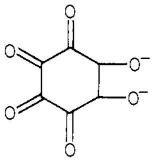
$H{=}CH_2$, C_6H_6, $C_6H_5CH_3$, CH_4, n-C_5H_{12}, CH_2Cl_2, N_2, He, or Ar. In fact, the CO adsorption on MgO could be performed (to form the radical anion species) in the presence of these reagents. For example, if thermally activated MgO was submerged in $C_6H_5CH_3$ followed by CO addition, normal behavior was observed (color formation and radical anion formation).

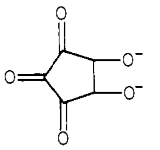
Proposed Structural Assignments for Radical Anion and Dianion Species. Our previous report[28] and that of Cordischi and co-workers[21] appeared almost simultaneously, both independently concluding that the CO radical species on MgO was the dimer radical anion. However, in light of new findings, we now believe

$$\frac{[\cdot O{-}C{=}C{-}O^-]}{MgO}$$

that the major radical species is the rhodizonate trianion and not the $C_2O_2^-\cdot$ as first thought. Our reasoning is discussed below.

Chemical Considerations. Recall the colors generated when thermally activated MgO is exposed to CO. The red color is not directly due to the radical anion species. Zecchina, Stone, and co-workers[22,23] proposed the existence of large CO ring telomers as dianions, including four-, five-, and six-membered rings.[27] It is interesting that the five- and six-membered species (croconate and rhodizonate) are yellow and red, respectively. It seems reasonable that these species are responsible for the colors generated on MgO and perhaps CaO as well. Furthermore, we have shown that red CO/MgO can be converted to yellow CO/MgO by heating under vacuum, and earlier discussion pointed out that under basic conditions rhodizonic acid will convert to croconic acid.[13,14] We also have shown that red CO/MgO is much more thermally stable to color change under a CO atmosphere. Thus, gaseous CO inhibits the red → yellow thermal conversion, supporting the notion that the process involved is the $C_6O_6^{2-} \rightarrow C_5O_5^{2-} + CO$ conversion. Alternatively, both $C_6O_6^{2-}$ and $C_5O_5^{2-}$ are present simultaneously, but $C_6O_6^{2-}$ is selectively destroyed by heat in the absence of CO. The yellow coloration of the $C_5O_5^{2-}$ would then predominate.


rhodizonate dianion
(red)


croconate dianion
(yellow)

As mentioned previously, several chemical reagents also cause a red → yellow conversion on addition to the red CO/MgO system. Carbon dioxide, HCl, NH_3, and O_2 (gradual addition) all forced this color change. It is possible that these materials destabilize the $C_6O_6^{2-}$ system by nearby adsorption, just as they destabilize the radical anion system. Thus, they could either force the $C_6O_6^{2-} \rightarrow C_5O_5^{2-}$ conversion or selectively completely destroy the $C_6O_6^{2-}$ system but not the $C_5O_5^{2-}$ system.

It is important to reemphasize that whenever color formation occurred, radical anion formation also occurred. This indicates that either an identical or very similar surface process is required for the formation of the oxocarbon colored species and the radical anion species (which are clearly different species). Thus, the acquisition of extra electrons by these CO telomers from the surface of the MgO or CaO probably occurs in very similar ways. (The source of electrons on the MgO or CaO surface is believed to be due to defects, possibly Mg^{2+} deficiencies. The nature of these surface sites is discussed in more detail elsewhere.)[34] It even seems likely that the colored species are precursors of the radical anions, based on the fact that the color always precedes formation of the radical anions.

Table I. Summary of g and A Values for Pertinent Radical Anions

radical	$g_{av(iso)}$	$A_{^{13}C}$, G	ref
$C_2O_2^-\cdot$(matrix)	2.0136	14.9	9
$C_6O_6^{3-}\cdot$(solution)	2.00457		18
$C_6O_6^{3-}\cdot$(adsorbed)	2.0043	11.8	this work

Table II. Comparison of Radical Anion g_{iso} Values on the Surfaces of MgO and CaO vs. in Solution

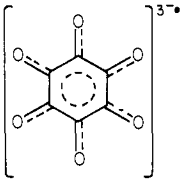
anion radical	MgO	CaO	soln	ref
nitrobenzene	2.0045	2.0045	2.0044	36
benzoquinone	2.0046	2.0046	2.00468	37
anthracene	2.0027	2.0028	2.0027	37
CO_2	2.0006		2.0007	35, 38

ESR Spectral Considerations Including Computer Simulations. As previously pointed out, $C_2O_2^-\cdot Li^+$ has been prepared in a frozen matrix, and ESR parameters have been recorded as $g_{\parallel} = 2.0134$, $g_{\perp} = 2.0138$,[9] and $A_{^{13}C} = 14.9$ G. Although our CO/MgO radical has a similar ^{13}C splitting constant, the g value is substantially different; thus g_{av} for matrix isolated $C_2O_2^-\cdot = 2.0136$, while our adsorbed system yields $g_{av} = 2.0043$ and $A_{^{13}C} = 11.8$ G. These differences caused us to question Cordischi's and our previous assignments regarding adsorbed $C_2O_2^-\cdot$. Furthermore, the similarities in g values of virtually all the adsorbed radical anions we have observed on MgO or CaO are very similar, even with added reagents, and g_{av} only varies from 2.0043 to 2.0047 for all systems. Compare with this the g_{av} for $C_2O_2^-\cdot$ (2.0136) and $CO_2^-\cdot$ (2.0006, $A_{^{13}C} > 180$ G).[35] This indicates that whatever the adsorbed CO radical anions are under various conditions, they are very similar in nature and probably are not $C_2O_2^-\cdot$ (see Table I for a summary).

We turned to computer simulation hoping to clarify the situation. However, after extensive work with two-, four-, and six-^{13}C splitting systems we again came to the conclusion that by far the best fit was found by using a two-^{13}C spin system.[28] Thus, the dichotomy exists that the simulation supports a two-carbon system, but g value and chemical "evidence–intuition" predict a larger telomer system.

The next obvious point to consider is whether adsorption can cause a significant g-value shift as opposed to solution or matrix isolation experiments. A literature search showed that a variety of radical anions formed and adsorbed on the surface of MgO and CaO exhibit g values essentially the same as in solution. Table II illustrates these data, which dictate that we must consider the g value as a very important parameter.

Considering that the radical anion's ESR spectrum can be perturbed but not grossly changed by: (a) the method of thermal activation of MgO or CaO before CO addition, (b) addition of a variety of chemical reagents to the radical anion, and (c) thermal treatment of the CO/MgO or CO/CaO systems, we propose that the radical anion must be fluxional species whose orientation on the surface of the MgO (or CaO) can be relatively easily changed. A telomeric ring system would fit this criterion. Furthermore, there is a known radical anion ring system that possesses the correct g value, and it is the rhodizonate trianion previously described by Patton and West.[18] We propose that this trianion


5, $g_{iso} = 2.004\,57$

exists on the surface of MgO or CaO in forms that, on an ESR

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(34) R. M. Morris and K. J. Klabunde, *Inorg. Chem.* **22**, 682 (1983).

(35) P. Meriaudeau, J. C. Vedrine, Y. Ben Taarit, and C. Naccache, *J. Chem. Soc., Faraday Trans. 1*, 71, 736 (1975).

(36) H. Hosaka, T. Fujiuaro, and K. Meguro, *Bull. Chem. Soc. Jpn.*, 14, 2616 (1971).

(37) B. G. Segal, M. Kaplan, and G. K. Frankel, *J. Chem. Phys.*, 43, 4191 (1965).

(38) D. W. Oven and D. H. Wiffen, *Mol. Phys.*, 4, 135 (1961).

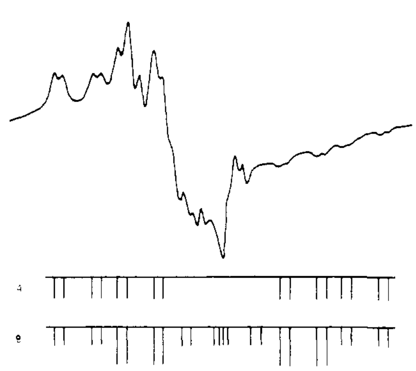
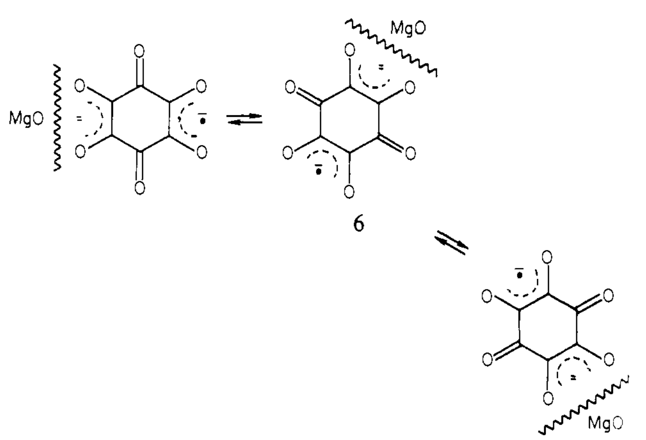


Figure 14. Stick models proposing (A) four and (B) five carbon-13 atoms as a structure for radical.

time scale, have the unpaired electron magnetically interacting with only two-^{13}C atoms, as shown below:



To summarize our reasoning for this proposal: (1) the rhodizonate dianion is very likely an important diamagnetic species formed on MgO; (2) the *g* value matches that of $C_6O_6^{3-}\cdot$; (3) the fluxional character this radical anion could possess may explain why the ESR spectra show perturbations under certain conditions where it is apparent that the number of splitting carbons has changed; (4) computer simulation predicts a two-carbon splitting system; (5) according to Hückel rule the $C_6O_6^{3-}\cdot$ system could be nonaromatic, so a localized bonding mode, especially in the adsorbed state, would be favorable; (6) although it would be predicted that other carbons in the localized $C_6O_6^{3-}\cdot$ system would also magnetically interact, they would do so to a smaller degree (since we are dealing with a anisotropic powder system, if the splittings by these other carbons were <2–3 G, they would be difficult to detect); (7) the conversion of the starting radical anion on MgO to a very complex radical by O_2 treatment (see previous discussion) would be difficult to rationalize with only a two-carbon splitting system (A larger number of magnetically interacting carbons would be needed to explain such a complex system.); (8) the timing of formation requires that the colored dianion species form first followed by formation of $C_6O_6^{3-}\cdot$; and this seems logical in that some time may be required for positive hole/electron migration in the bulk to form the trianion, or alternatively, for the proper site for a three-electron reduction to be found or formed.

Spin Density Calculations. Some calculations intended to describe the electron-density distributions in adsorbed $C_6O_6^{3-}\cdot$ were carried out using the experimentally observed $g_1 = 2.0058$, $g_2 = 2.0048$, and $g_3 = 2.0023$ and (^{13}C) $a_1 = 7.9$ G, $a_2 = 8.2$, and $a_3 = 19.3$ G. Since g_3 deviates the least from the free-electron value (2.00232), g_3 is assigned along the *z* axis. The *x* and *y* axes are assigned g_1 and g_2, respectively. We note that a_z is quite large compared with a_x and a_y, which indicates that the unpaired spin density must reside almost totally in the $2P_z$ orbital.

The anisotropic hyperfine splitting tensor is determined by subtracting out the isotropic portion. By use of these parameters, the unpaired spin density on the carbon atom was calculated to be about 1% in the 2S orbital, 0.3% in the $2P_y$, and 12% in the $2P_z$. This corresponds to a total of 26% unpaired spin density for two carbons. The rest (74%) we assume is located on the two oxygen atoms.

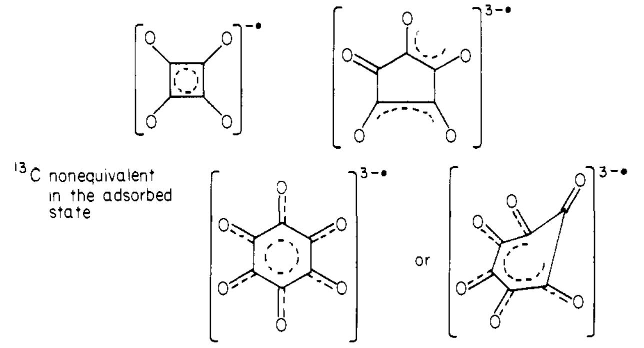
Structural Assignments for Minor Radical Anions. As radical anion **6** is perturbed by heating, O_2 addition, or other means, it apparently changes its adsorbed state to a different conformation, or loses CO to go to smaller ring system. These perturbations in conformation do not change the *g* values or ^{13}C splitting values significantly, and so no gross spectral changes are apparent.

The radical species observed in our work by using low-temperature activated MgO or by treating **6** with limited amounts of O_2 appears to be the same radical Cordischi and co-workers[21] formed by treatment of their radical (which they propose as $C_2O_2^-\cdot$ and we propose is $C_6O_6^{3-}\cdot$) with NO (which we now label as **7**). They proposed a four nonequivalent carbon atom species. Figure 14 illustrates the spectrum in question and shows the splitting that would be expected for a four- or five-carbon (^{13}C) model (nonequivalent carbons in the four-carbon model and two strongly interacting equivalent and three weakly interacting nonequivalent carbons in the five-carbon model are assumed). Neither system predicts exactly what is observed.

The g_{iso} values for the cyclic monoanion radicals are $C_4O_4^-\cdot$ = 2.00584, $C_5O_5^-\cdot$ 2.00624, and $C_6O_6^-\cdot$ 2.00652.[18] Our radical system (**7**) exhibits a $g_{av} = 2.0054$, which most closely matches that of the $C_4O_4^-\cdot$ species, but the match is not particularly good. Unfortunately the ESR spectra of $C_4O_4^{3-}\cdot$ and $C_5O_5^{3-}\cdot$ have not been reported (we made attempts at preparing them in solution, by electrochemical methods, but were not successful).

There are two pieces of evidence suggesting that radical **7** is actually the same as **6** but in a different adsorbed conformational state. The thermal stabilities of **7** and **6** are similar (175 °C for **7** and 225 °C for **6**). Larger differences might be expected for $C_4O_4^-\cdot$ vs. $C_6O_6^{3-}\cdot$. Also, the *g* values and splitting parameters are similar.

Thus, there are at least three likely possibilities for the structure of **7**, none of which are perfectly satisfying. These are

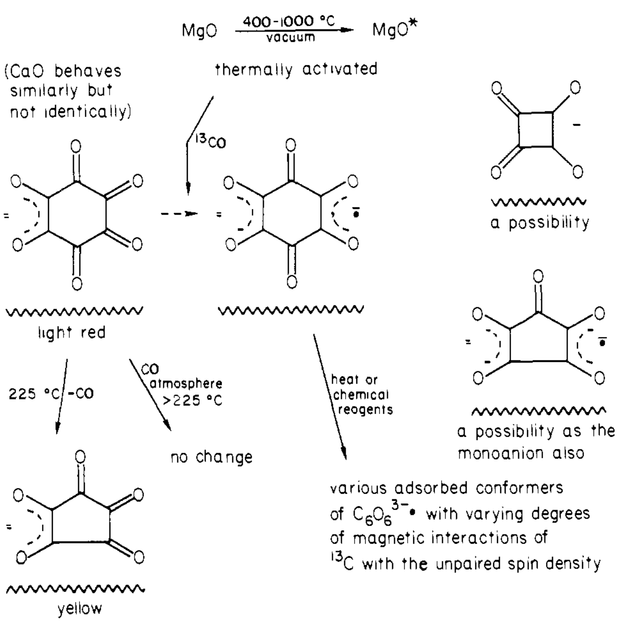


Other radical anions observed upon treatment of **6** with various reagents are probably just different conformers of **6** where fewer or more carbons magnetically interact with the unpaired spin density. The *g* values observed change very little from those observed for **6**, thermal stabilities are very similar, and ^{13}C splitting constants do not vary much. We draw similar conclusions about the radical anions on CaO. The most important species is probably the rhodizonate trianion radical, and perturbations of this by different thermal activation of CaO, thermal treatments of the trianion, or addition of reagents simply cause perturbations of the surface adsorption state of **6**.

Conclusions

Adsorption of CO onto thermally activated MgO or CaO leads to the formation of a variety of adsorbed dianion (diamagnetic and colored) species. The rhodizonate dianion (red) is the most likely species formed on high temperature (600–1000 °C) activated MgO and is formed immediately. This $C_6O_6^{2-}$ species can be converted to $C_5O_5^{2-}$ (yellow) by thermal treatment or by treatment with several chemical reagents. Also, the $C_5O_5^{2-}$ species is favored by the use of low-temperature (400–500 °C) thermally activated MgO or by use of CaO.

Scheme I



Adsorption of CO onto thermally activated MgO or CaO also leads to the formation of several adsorbed, paramagnetic radical anions. Although these species may be colored, their concentrations are much lower than the dianion species discussed above, and therefore color is not indicative of their presence (2–10% of the adsorbed CO yield paramagnetic species). The formation of the anion radicals is preceded by formation of the colored dianaions.

A variety of considerations, including ESR spectral evidence, spectral computer simulations, and chemical treatments, lead us to the conclusion that the most common radical anion is the $C_6O_6^{3-}\cdot$ species, which is probably formed from $C_6O_6^{2-}$. The surface adsorption state of this species is such that only two carbons strongly interact with the unpaired spin density. Upon treatment of this trianion radical with heat, oxygen (slow addition), CO_2, H_2O, HCl, or NH_3 it is converted to a different adsorbed state where different magnetic interactions occurs but in which no gross chemical changes have occurred (new bond formations or bond cleavages). It is also possible that some smaller ring species form. These ideas are illustrated in Scheme I.

Apparently the added reagents adsorb on the MgO or CaO surface near the $C_6O_6^{3-}\cdot$ species and cause a change in its conformational state, either by changing the electronic properties of the basic surface or simply by crowding the $C_6O_6^{3-}\cdot$ species. Neither the dianions or trianions are affected by adding relatively nonreactive substances (at 25 °C) such as H_2, CH_4, N_2, C_2H_4, or $C_6H_5CH_3$. In fact, the activated MgO can be placed in a bath of pure toluene followed by CO addition, and both colored dianions as well as paramagnetic trianions form without toluene interference.

Experimental Section

Materials. The preparation of MgO samples has been described previously.[28,34] A single source of calcium oxide was obtained from ROC/RIC listed as 99.99% pure. CO (Linde, 99.999%) was passed through a 77 K cold trap just prior to adsorption on the oxide samples. ^{13}CO (Prochem Isotopes, 98% ^{13}CO, 2% ^{12}Co) was passed over a freshly regenerated BASF-R3-11 deoxygenation catalyst and then through a −196 °C trap just prior to adsorption.

EPR Spectroscopy. Two spectrometers were used, a Bruker ER-420/10V and a Varian V-4502. The Bruker instrument was used to obtain all ^{13}C data, and experimental parameters have been reported previously.[28]

Sample Preparations. The oxide samples were washed with boiling distilled water for 1 h, recovered by hot filtration, and dried in air at 110 °C for ~6 h, and the samples were stored in vials awaiting thermal activation. Each oxide sample was chopped (not ground since grinding produced higher concentrations of paramagnetic defects) into small pieces <1.5 mm. About 100 mg was placed in a 10–15-cm quartz cell equipped with a graded Pyrex seal to a high vacuum stopcock (4 mm). The cell was evacuated slowly and heating was begun very slowly. About 2.5 h was needed to attain 380–400 °C, and then several more hours were needed to slowly reach the desired temperature. The extremely slow heating was necessary to avoid violent degassing of the oxide sample. The desired temperature was maintained for about 14 h and followed by cooling to room temperature. Typical pressures at the conclusion of this process were 2 × 10^{-6} torr.

When large samples of thermally activated MgO or CaO were required, a special apparatus was necessary. A quartz bulb with a graded Pyrex seal was connected to a glass frit and then to the vacuum system. A frit bypass tube with a stopcock was also necessary. Upon heating of the sample (up to 2 g could be used) the glass frit prevented loss of sample to the vacuum system on the numerous occasions that violent degassing (powder flying about) took place. Very slow heating was necessary, and after the system had stabilized the by pass valve was opened. Pressures about 1 × 10^{-5} torr could be attained.

After cooling to room temperature the oxide samples were treated with ^{12}CO or ^{13}CO, usually at 150 torr. The CO atmosphere usually remained over the sample for several weeks as radical anion growth took place. Then ESR studies were carried out, the CO atmosphere was removed, and desired chemical reagents were added, always in excess, on a vacuum system.

Acknowledgment. Support of the Department of Energy and the DOW Chemical Co. is acknowledged with gratitude.

Registry No. CO, 630-08-0; CaO, 1305-78-8; MgO, 1309-48-4; $C_6O_6^{2-}$, 28737-41-9; $C_5O_5^{2-}$, 15110-70-0.

A New Type of Oscillating Reaction: Air Oxidation of Benzaldehyde

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Contribution from the Petrochemicals Department, E. I. du Pont de Nemours & Company, Experimental Station, Wilmington, Delaware 19898. *Received September 1, 1982*

Abstract: During the air autoxidation of benzaldehyde catalyzed by cobalt and bromide, the solution oscillates between pink and dark brown. The color changes correspond to redox potential changes and can occur for several hours.

Several homogeneous liquid-phase reactions that oscillate between two states have been studied recently. The underlying mechanism for this seemingly odd behavior is now understood for several of these reactions.[1,2] The most thoroughly studied types

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