

the ring plane has a time scale of the order of 10^{18} yr (ref. 9); it may be neglected. (4) Atmospheric drag is eliminated because the gas molecules are mopped up by the ring¹². (5) Micrometeorite erosion at the lunar rate ($0.2\text{--}0.8\text{ mm Myr}^{-1}$) would severely limit the lifetimes of the particles; but most of the erosion in the lunar case is due to craters $>400\text{ }\mu\text{m}$ in diameter¹³; the small size of the ring particles has a large effect in limiting damage. (6) Rotational bursting due to windmill effects of radiation pressure¹⁴ will be damped by collisions. (7) Thrust effects due to photon recoil¹⁵ will also be damped by collisions. (8) The Poynting–Robertson effect would cancel out around a geocentric orbit except for the fact that part of the orbit lies in the Earth's shadow. The net effect is an outward motion (if the sense of the orbit motion is direct) which probably limits the lifetime of the ring to a few million years.

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Note added in proof: Ruderman and Truran¹⁶ have similarly suggested that dust ejected from the Moon may cause sudden climatic changes on the Earth.

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1. Wolfe, J. A. *Am. Scient.* **66**, 694–703 (1978).
2. Glass, B. P. & Zwart, M. J. in *Proc. Symp. Stratigraphic Micropaleontology of the Atlantic Basin and Borderlands* (ed. Swain, F. W.) 553–567 (Elsevier, New York, 1977).
3. Glass, B. P., Swincki, M. B. & Zwart, P. A. *Lunar planet. Sci.* **10**, 434–436 (1979).
4. Darwin, G. H. *Scientific Papers Vol. 2*, 208–302 (Cambridge University Press, 1908).
5. Brosche, P. & Sündermann, J. (eds) *Tidal Friction and the Earth's Rotation* (Springer, New York, 1978).
6. Urey, H. C. *Nature* **242**, 32–33 (1973).
7. O'Keefe, J. A. *Tektites and their Origin*, 180–187 (Elsevier, New York, 1976).
8. Jeffreys, H. *Mon. Not. R. astr. Soc.* **107**, 263–267 (1947).
9. Brahic, A. *Astr. Astrophys.* **54**, 895–907 (1977).
10. Glass, B. P. & Zwart, M. J. *Bull. geol. Soc. Am.* **90**, 595–602 (1979).
11. Goldreich, P. & Tremaine, S. *Icarus* **34**, 240–253 (1978).
12. Opp, A. G. *Science* **207**, 401–403 (1980).
13. Comstock, G. M. *Lunar Science VIII*, 202–204 (Lunar Science Institute, Houston, 1977).
14. Paddack, S. J. *J. geophys. Res.* **74**, 4379–4381 (1969).
15. Jacchia, L. in *The Moon, Meteorites and Comets* (eds Middlehurst, B. M. & Kuiper, G. P.) 783–784 (University of Chicago Press, Chicago, 1963).
16. Ruderman, M. & Truran, J. W. *Nature* **284**, 328–329 (1980).

Bivalent spectator oxo bonds in metathesis and epoxidation alkenes

Anthony K. Rapp & William A. Goddard III

Arthur Amos Noyes Laboratory of Chemical Physics, California Institute of Technology, Pasadena, California 91125

Several studies suggest the importance of oxygen in the reactive intermediates for alkene metathesis,



and of additional metal=oxo bonds in epoxidations,

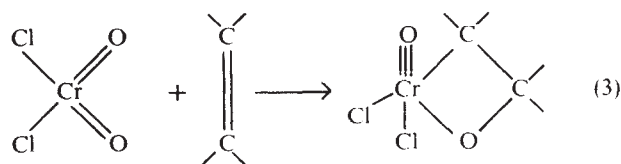


For example: (1) catalytic amounts of oxygen were found to be essential for the formation of a stable metathesis catalyst in the $\text{WCl}_6/\text{C}_2\text{H}_5\text{AlCl}_2$ system¹; (2) alkene epoxidation (and general oxidation) reactants such as CrCl_2O_2 , OsO_4 , and SeO_2 all have at least two oxygen ligands²; and (3) recently Osborn (personal communication) has described an Mo=oxo carbene as an effective metathesis catalyst. From extensive *ab initio* theoretical studies of Cr and Mo complexes, we show here that the presence of spectator metal=oxo bonds drives the formation of metallocycles, thereby playing a crucial role in the chemistry.

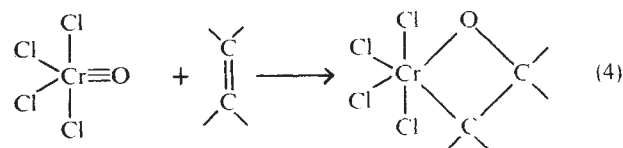
The special role of the oxo group is illustrated by comparing the oxo bond energy of $\text{Cl}_4\text{Cr}=\text{O}$ (343 kJ mol^{-1}) with the oxo bond energy of $\text{Cl}_2\text{Cr}=\overset{\text{O}}{\text{C}}$ (213 kJ mol^{-1}). (Calculated numbers are based on *ab initio* calculations using valence double zeta basis sets and including electron correlation (generalized valence bond plus configuration

interaction as in ref. 3). Estimated vibrational frequencies were used to calculate ΔH (0K) from the theoretical energy differences. Standard approaches⁴ were used to estimate ΔS and the correction of ΔH to 25°C .) The origin of this difference is that in $\text{Cl}_4\text{Cr}=\text{O}$ there are two $d\pi$ orbitals on the Cr available for forming π bonds to the oxygen, leading to a triple bond (analogous to $\text{C}\equiv\text{O}$). However, in $\text{Cl}_2\text{Cr}=\overset{\text{O}}{\text{C}}$ the corresponding d orbitals are each used in the π bond for different oxo bonds, leading to two double bonds (analogous to $\text{O}=\text{C}=\text{O}$ or a ketone, $\text{R}_2\text{C}=\text{O}$). Thus the metal–oxo bond is dual-valent, existing in two alternative forms depending on the other ligands. The orbital character of the oxo double bond is as in a ketone⁵ with a singly-occupied $\text{O}p\sigma$ orbital paired with the singly-occupied metal $d\sigma$ orbital, a singly-occupied $\text{O}p\pi_x$ orbital paired with a singly-occupied $d\pi_x$ orbital and the remaining doubly-occupied $\text{O}p\pi_y$ pair nonbonding. For the oxo triple bond, the oxygen orbitals are oriented so as to have two π bonds with the $p\sigma$ pair of the oxygen coordinated with an empty metal $d\sigma$ orbital. In both cases the bonding is basically covalent with a small charge on the oxygen.

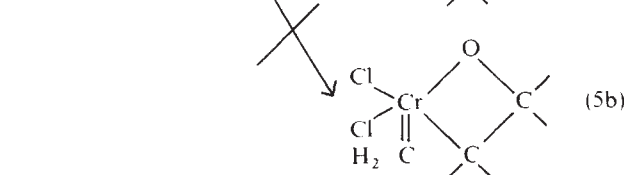
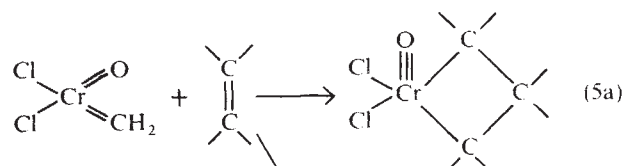
Addition of an alkene to Cl_2CrO_2 to form the metallocycle oxetane from one oxo bond allows the spectator oxo bond to convert from a double bond to a triple bond, thereby providing a 130 kJ mol^{-1} push towards formation of the metallocycle (calculated $\Delta H = -113\text{ kJ mol}^{-1}$, $\Delta G(25^\circ\text{C}) = -63\text{ kJ mol}^{-1}$),



For a single oxo bond, this process is doubly bad; here there is no spectator oxo bond to drive the metallocyclization and one must also add across an oxo triple bond (calculated $\Delta G(25^\circ\text{C}) = +300\text{ kJ mol}^{-1}$),



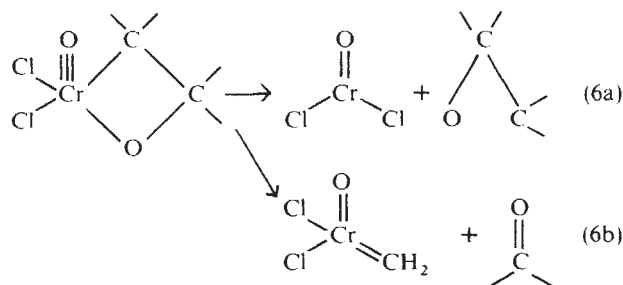
An oxo-carbene behaves similarly,



with metallocyclobutane formation favoured by conversion of the spectator oxo bond to a triple bond (calculated $\Delta G(25^\circ\text{C}) = -42\text{ kJ mol}^{-1}$), whereas metallocyclohexane formation has no such driving force and is significantly uphill (calculated $\Delta G(25^\circ\text{C}) = +50\text{ kJ mol}^{-1}$).

The same effects are found from calculations on Mo [$\Delta G = -105\text{ kJ mol}^{-1}$, for reaction (3), $\Delta G = -84\text{ kJ mol}^{-1}$ for reaction (5a)] and should occur also for W. The essential difference between Cr and Mo (or W) is in the decomposition products of the metallocycles and arises from the change in the

strength of metal carbon or metal oxygen bonds. For $\text{Cl}_4\text{Mo}\equiv\text{O}$ we find an oxo bond energy of 456 kJ mol^{-1} , whereas for $\text{Cl}_4\text{Cr}\equiv\text{O}$ we find 343 kJ mol^{-1} . For example, for Cr metalocycle oxetane we find that reductive elimination dominates [reaction (6a)], whereas for Mo, metal carbene formation is competitive [reaction (6b)]. Similarly, Cr metalocyclobutane reductively eliminates propane, whereas for Mo, the metathesis product is formed,



We suggest that this dual-valent character of the spectator metal-oxo bond may be generally useful for designing catalysts or substrates to promote reactions involving metalocycle formation.

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1. Mocella, M. T., Rovner, R. & Muetterties, E. L. *J. Am. chem. Soc.* **98**, 4689 (1976).
2. Sharpless, K. B., Teranishi, A. Y. & Bäckvall, J. E. *J. Am. chem. Soc.* **99**, 3120 (1977).
3. Harding, L. B. & Goddard III, W. A. *J. Am. chem. Soc.* **99**, 4520 (1977).
4. Benson, S. W. *Thermochemical Kinetics* (Wiley, New York, 1976).
5. Harding, L. B. & Goddard III, W. A. *J. Am. chem. Soc.* **97**, 6293 (1975).

Observations of nitrous acid in an urban atmosphere by differential optical absorption

U. Platt*, D. Perner*, G. W. Harris†, A. M. Winer† & J. N. Pitts Jr†

*Kernforschungsanlage Jülich GmbH, Institut für Chemie 3: Atmosphärische Chemie, Postfach 1913, D-5170 Jülich, FRG

†Statewide Air Pollution Research Center and Department of Chemistry, University of California, Riverside, California 92521

In the past decade, increasing attention has been paid to the role of nitrous acid (HONO) in the polluted troposphere, primarily as an initiator of photochemical air pollution¹ through its photodissociation by solar UV radiation into hydroxyl radicals and NO. The OH radical may subsequently attack organics starting a chain photooxidation which leads to the production of O₃, peroxyacetyl nitrate and many other secondary pollutants. Measurements of the concentration of HONO, especially in the early morning, are needed to establish the initial conditions to be used in computer kinetic models of photochemical oxidant formation²⁻⁴. From laboratory studies, it has been suggested that nitrous acid may also be a precursor to the possible formation of nitrosamines by reaction with simple secondary and tertiary amines in urban air⁵, or *in vivo* following inhalation. We report here a series of observations, at Riverside and Claremont, California, of the gradual buildup of HONO during the night and its rapid decay after sunrise. These, we believe, represent the first unequivocal measurements of HONO reported for a major urban air basin impacted by photochemical air pollution.

Nitrous acid was detected and monitored using the long path differential UV absorption technique described by Platt *et al.*⁶. The optical system in the present experiments used a 0.3 m McPherson spectrograph with a 600 grooves mm^{-1} grating blazed at 500 nm (giving a dispersion of 5.3 nm per mm). A spectral region 38 nm wide was scanned by exit slits etched in a thin metal disk, which rotated in the focal plane of the instrument.

The light signals were received by a photomultiplier (EMI 9656Q) and averaged by a DEC PDP11 MINC microcomputer. The scan rate of 105 Hz provided by the rotating disk was fast enough to eliminate unwanted signal variations. Absorption lines with optical densities as low as 10^{-4} (base 10) could be detected. We used the HONO absorption lines at 354.1 and 368.1 nm which have differential absorption cross-sections (D.P., unpublished data) of 4.7×10^{-19} and $3.8 \times 10^{-19} \text{ cm}^2$ respectively. Before measuring the optical density of atmospheric HONO bands, nearby NO₂ bands were eliminated by the subtraction of a suitably weighted NO₂ reference spectrum. For the 354.1 nm band the minimum detectable optical density corresponded to 0.28 p.p.b. (parts per 10⁹) HONO using a 970 m lightpath. The light source was a 500-W Xe high pressure lamp (Hanovia 959C).

The night-time buildup of HONO was measured during August and September 1979 (see Table 1) in the Los Angeles air basin at Riverside (a downwind receptor site) and at Claremont (a midbasin site). Figure 1 shows the development of HONO bands during the night of 4-5 August and their decay after sunrise. The observed bands agree well in shape and position with the reference spectrum shown. Additional broad absorption features at ~ 352 and 360 nm are present

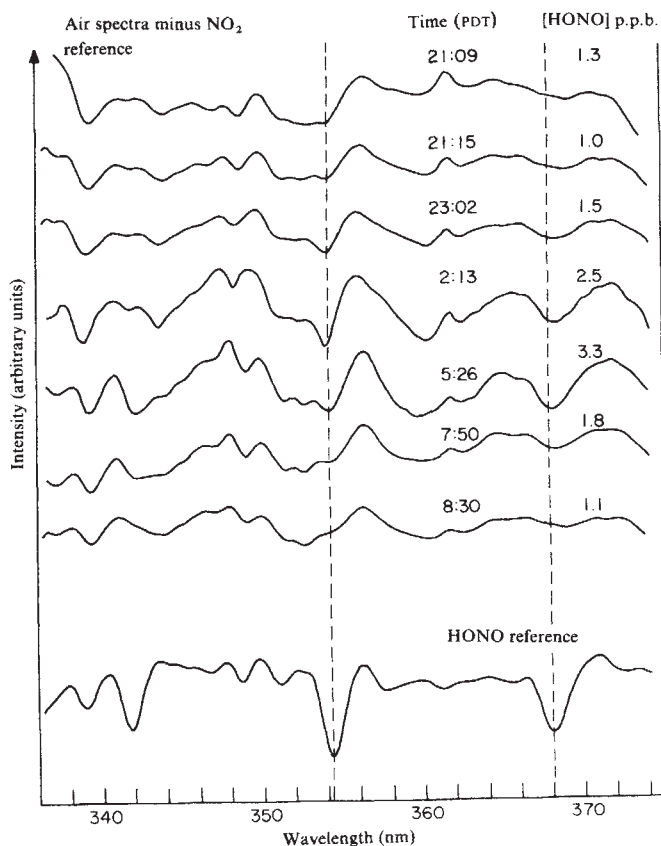


Fig. 1 Air spectra from which absorptions due to NO₂ have been subtracted. 4-5 August 1979, Riverside, California. The lowest trace is a HONO reference spectrum.