Reflection Infrared Studies of Zinc Dialkyl Dithiophosphate Films Adsorbed on Metal Surfaces

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THE RECENT development of the reflection infrared technique (2) whereby spectra of films as thin as monolayers could be observed appeared to offer a new approach to the study of boundary lubricant films. Zinc dialkyl dithiophosphates are known to possess outstanding extreme pressure properties as demonstrated by their ability to control valve train wear in today's high compression engines (*6*). This work was undertaken in an attempt to understand the film-forming properties of this type of additive and to deveolp a possible relationship between film composition and additive function.

Information about the functions of zinc dialkyl dithiophosphates in lubricants has been summarized recently by Scanley and Larson (*6*). Briefly, zinc dialkyl dithiophosphates reduce lubricant oxidation by decomposition of peroxides and reduce bearing corrosion and wear or "scuff" by the formation of protective films on metal surfaces.

Radioactive tracer techniques have been used to study the nature of these protective films (*3, 4*). This work has demonstrated the formation of multilayer films on metal surfaces and provided accurate deteriminations of zinc, phosphorus, and sulfur in such films. The results show that the additive undergoes chemical reaction in forming films but they do not establish the molecular composition of the film components.

The present work constitutes primarily an infrared study of such films using the reflection technique. Electron diffraction and x-ray fluorescence techniques aided in the interpretation of the infrared data. These films may contain a multiplicity of components, and the composition and amount of film in any given experiment are affected by many variables, including the metal, solvent, temperature, and structure of the zinc dialkyl dithiophosphate.

EXPERIMENTAL

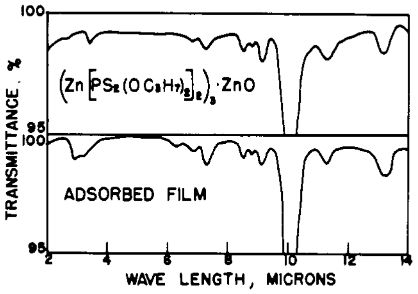
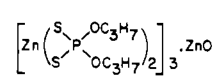


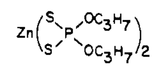
Figure 1. Spectra of basic zinc diisopropyl dithiophosphate and of adsorbed films

Sample Preparation. Films were formed on polished metal mirrors which were immersed in hydrocarbon solutions containing the zinc dialkyl dithiophosphate additive. The metal samples, either fine silver (Handy and Harmon, 99% pure) or SAE 1020 cold-rolled steel, 2 × 1½ × ⅛ inches in size, were polished to a mirror finish on one large face with a polishing wheel covered with kitten-ear polishing cloth using Linde alumina (Type B-5125) as the abrasive. To clean the mirrors they were repolished on the wheel for a few minutes between experiments. Following this cleaning procedure the mirrors were rinsed thoroughly with distilled water, while being rubbed with a clean cotton swab to aid in removing the alumina from the surface. They were dried in a warm air stream from a hair dryer. At all stages after the cleaning step, the mirrors were handled with a thin platinum wire hooked through a small hole drilled near the upper edge of the mirror. In most of the work, films were produced on sample mirrors by immersing the mirrors for a measured time at a measured temperature in a beaker containing a hydrocarbon solution of zinc dialkyl dithiophosphate. Upon removal from the solution the mirrors were rinsed twice using *n*-heptane (Mathieson practical grade) freshly percolated through silica gel for each rinse. Since the zinc additive is soluble in *n*-heptane, this ensured that only adsorbed or heptane-insoluble material remained on the mirrors. Two zinc additives were used. One was a sample of basic zinc diisopropyl dithiophosphate, m.p. 204–6° C., having the structural formula



$$\left[\mathrm{Zn}\left(\mathrm{S_2P(OC_3H_7)_2}\right)_2\right]_3\cdot\mathrm{ZnO}$$

The other sample was the neutral zinc salt, melting point 137°–8° C., having the structural formula



$$\mathrm{Zn}\left(\mathrm{S_2P(OC_3H_7)_2}\right)_2$$

These compounds will be referred to as basis *Z* and neutral *Z* in the following discussions.

The possibility that water might be involved in the reactions of these materials was recognized. The solvents and zinc additives used were initially dry, but no special precautions were taken to exclude pickup of moisture from the atmosphere. Results indicate that under the conditions of these experiments, water was not an important reactant.

A few films will be discussed which were prepared by rubbing the zinc additive on the mirrors with degreased cotton, followed by the heptane rinse.

Apparatus. Infrared spectra of the films on the sample mirrors were obtained using the modified infrared apparatus described previously for the study of very thin films on reflecting surfaces (*2*). The instrument is a Perkin-Elmer Model 21 infrared spectrophotometer equipped with electronic transmission scale expansion, silver chloride polarizer in front of the detector, and the special sample mirror arrangement described previously.

Zinc content of selected films was measured by x-ray fluorescence spectroscopy in a manner described by Loeser, Wiquist, and Twiss (*4*). A Norelco three-position x-ray spectrograph, Type No. 52254, with a tungsten target irradiating tube, a LiF analyzing crystal, and a scintillation counter was used. Calibrations were made with films of zinc stearate prepared by the Blodgett (*1*) method.

Electron diffraction patterns of selected films were obtained by reflection using a noncommercial electron diffraction camera operating at 40 kv. and 45-cm. sample-to-plate distance.

RESULTS AND DISCUSSION

Zinc Oxide Films. Figure 1 shows a spectrum of a heptane-insoluble film produced on silver mirrors immersed for 17 hours at 25° C. in a heptane solution containing 1×10^{-3} gram per ml. of basic *Z*. The upper curve shows a spectrum of basic *Z*. The spectrum of the film has all the bands which are present in the original basic *Z*, and the band positions are unchanged. From this, we conclude that the film contains basic *Z* or a material very similar structurally to basic *Z*. In accord with the results of Furey and Kunc (*3*), the intensities of the bands indicate that the amount of basic *Z* in the film is considerably in excess of a monolayer. The spectrum supplies no explanation why the film material is heptane-insoluble.

Spectra of films formed on mirrors immersed in cetane solutions of basic *Z* were qualitatively similar to the spectra of films formed from heptane solutions. However, the bands were less strong for the films formed from cetane solutions than for those from heptane.

Table I shows analytical data for a number of films formed on silver and on steel mirrors from cetane solutions of basic *Z*. The concentration of basic *Z* in the films was determined from the intensity of the 10.0-micron band. The total zinc concentration in the films was determined by x-ray fluorescence spectroscopy. The results in Table I show that most of the zinc is present in some form other than basic *Z*., which does not produce appreciable infrared absorption in the 2-to 15-micron region.

Figure 2 shows a composite picture of electron diffraction patterns of an alumina-cleaned silver mirror, zinc oxide reference patterns, and silver and steel mirrors which had been immersed in heptane solutions of basic *Z* for 17 and 68 hours, respectively. The latter two patterns match the zinc oxide reference patterns well and are different from the pattern obtained from the alumina-cleaned mirror. The alumina-cleaned mirror gives a pattern characteristic of the alumina used for cleaning. It is concluded that the films contain crystalline zinc oxide. However, it is not possible by electron diffraction to determine how much zinc is present in this form.

The ZnO in these films can be converted to zinc stearate by immersing the film-coated mirrors in a cetane solution of stearic acid. This is illustrated for a typical case in Figure 3. ZnO, present either in small crystallites or in basic *Z*, is converted to zinc stearate by this treatment. The intensities of the zinc stearate bands so obtained provide a means for estimating the total ZnO in the films.

Data are plotted in Figure 4 which indicate that two components, basic *Z* and ZnO, account satisfactorily for the total zinc content in the films. The excess zinc in the films over that accounted for by basic *Z* is plotted as the abscissa. The points denoted by crosses represent the data given in Table I, where the total zinc content was determined by the x-ray fluorescence method. A linear relationship between basic *Z* in the films and excess zinc is indicated by the straight line drawn through these points. For the data indicated by circles, the excess zinc was calculated by subtracting the ZnO present in basic *Z* from the total ZnO as determined from the amount of zinc stearate formed. The fact that the circles fall near the same curve as the crosses indicates that the zinc in the films in excess of that present as basic *Z* is ZnO. Thus, these results support the picture that the film consists of only two components, basic *Z* and ZnO.

The straight-line relationship between the basic *Z* content of the films and the excess zinc in the films suggests the formation of a chemical compound between ZnO and basic *Z*. However, the existence of such a compound is contrary to the electron diffraction results which show crystalline ZnO. An alternative picture is that the film consists of small crystallites of ZnO with basic *Z* adsorbed on the ZnO surface. This picture is supported by the observation that the basic *Z* in a film produced by a 17-hour immersion in a heptane solution of basic *Z* is nearly completely removed by a 5-minute rinse in boiling acetone, while the crystalline ZnO in the film was not affected. A 3-minute immersion of the rinsed mirror in a solution of basic *Z* was sufficient to return the original amount of basic *Z* to the film. These results are consistent with the picture that the hot acetone rinse removes an adsorbed layer of basic *Z* and that this layer is rapidly readsorbed when the mirror is again immersed in a solution of basic *Z*.

Table I. Zinc Content of Films

Mirror Material	Adsorption Time, Hr.	Zn Atoms/Sq. Cm. × 10^{-14}	
		Basic Z^a	Total Zn
Silver	0.5	3.6	15
Silver	2	4.4	20
Silver	6	5.7	28
Silver	20	5.7	33
Steel	0.5	2.3	3
Steel	2	2.5	8
Steel	6	4.0	13
Steel	20	4.5	20

[a] Zn atoms in basic Z = 4 × basic Z concentration.

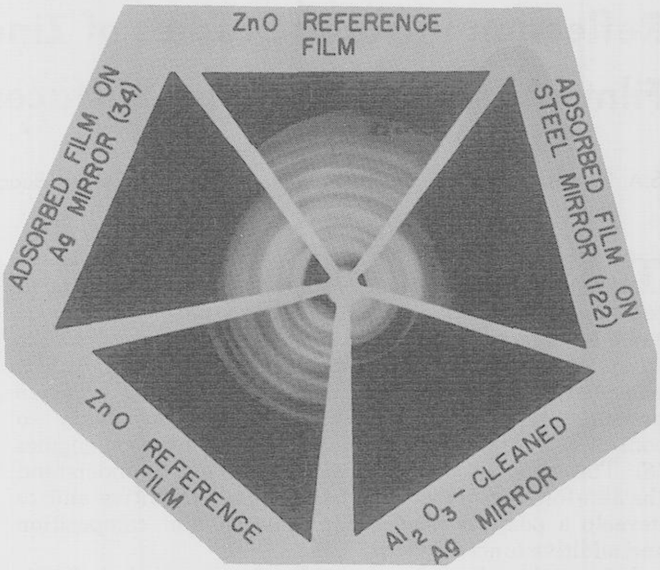


Figure 2. Comparison of electron diffraction patterns of adsorbed films and reference patterns

It seems reasonable to interpret the intercept in Figure 4 as the concentration of basic *Z* which adsorbs initially on the mirror surface before any ZnO crystals begin to build up. Then the slope represents the ratio in which basic *Z* and ZnO add to the film. If the added basic *Z* represents a monolayer adsorbed on ZnO crystallites, then a specific ratio of area to volume for the ZnO crystallites is implied. In the absence of any information on the crystal habit of the ZnO crystallites or the fraction of the surface available for adsorption of basic *Z*, the following calculation provides a rough estimate of the crystallite dimensions implied by this picture. The authors assumed an area of 200A^2 for the basic *Z* molecule as indicated by the intercept in Figure 4. The crystallites are assumed to be cubes so that all the available surface of both the mirror and ZnO crystallites is

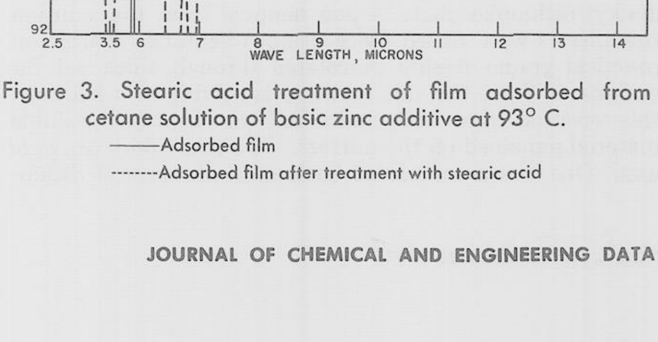


Figure 3. Stearic acid treatment of film adsorbed from cetane solution of basic zinc additive at 93° C.

——Adsorbed film

--------Adsorbed film after treatment with stearic acid covered with a monolayer of basic *Z*. The number of molecules of basic *Z* on a ZnO crystallite, *d* cm. on a side, is $6d^2/200 \times 10^{-16}$; the number of ZnO units in the crystallite is $6 \times 10^{23}\ d^3\ D/M$, where *D* is the density of ZnO and *M* is its molecular weight. This leads to a ratio of ZnO units in the crystallite to basic *Z* units on the surface of $1.38 \times 10^8 d$. The slope of the curve in Figure 4 indicates a ZnO-basic *Z* ratio of 26 and from the above calculation a crystallite dimension of 19A. For films formed from heptane solutions a ZnO-basic *Z* ratio of 63 was obtained, which implies a crystallite dimension of 46A. These crystallite sizes are in reasonable agreement with the sizes estimated from the line widths in the electron diffraction patterns.

The authors believe, on the basis of this data, that the films are built up in the following manner. When the clean mirror is immersed in the solution of basic *Z*, a monolayer of basic *Z* molecules rapidly adsorbs on the mirror surface. These molecules are in a state of kinetic equilibrium with molecules in solution, but at the concentration used here the surface is essentially covered with adsorbed molecules. The molecules of adsorbed basic *Z* decompose at a certain rate into ZnO and neutral *Z*. The molecules of neutral *Z* desorb and are replaced by more molecules of basic *Z*. The net result is a deposition of zinc oxide on the surface. The molecules of basic *Z* can adsorb on ZnO as well as on the mirror, producing the build-up of crystallites of ZnO on the mirror surface.

The inital observation that the film contained considerably in excess of a monolayer of basic *Z* led the authors to believe that the film was a multilayer, several molecules thick. However, it now appears that the molecules of basic *Z* in the film are present as a monolayer and appeared to be a multilayer because the surface area had been greatly increased by the deposition of ZnO crystallites.

This type of film is formed only from solutions of basic *Z* and not from neutral *Z*. Mirrors immersed in solutions of neutral *Z* at 25° C. rapidly adsorb approximately a monolayer of neutral *Z*, and the film does not increase.

Films Formed at Elevated Temperatures. Additional film components are produced at elevated temperatures. The spectra show that these additional components are formed from solutions of either neutral *Z* or basic *Z* at temperatures of 90° C. and higher. These components are studied most conveniently by using neutral *Z*, since then the results are not complicated by ZnO deposition. Curve *A* (Figure 5) shows the spectrum of a film formed on a silver mirror immersed for 1 hour in a cetane solution containing 1×10^{-3} gram per ml. of neutral *Z* at 149° C. Spectrum *B* is produced by a film formed on a silver mirror immersed for 17 hours in a cetane solution containing 1×10^{-3} gram per ml. of neutral *Z* and 6×10^{-4} gram per ml. of *tert*-butyl hydroperoxide at 25° C. The two spectra are very similar, except that the band intensities are considerably greater in *B*. The absorption bands at 7.25, 10.0, 11.3, and 13.2 microns are characteristic of neutral *Z*. The fact that the new bands near 3.0 and 8.7 microns are produced at elevated temperatures or at room temperature in the presence of a hydroperoxide suggests that they are due to a product of an oxidation reaction.

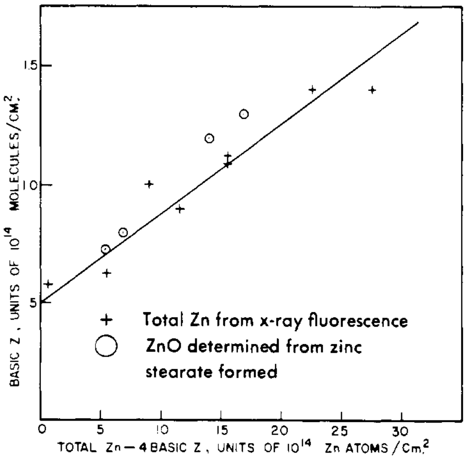


Figure 4. Relation between basic Z and excess zinc content in adsorbed films

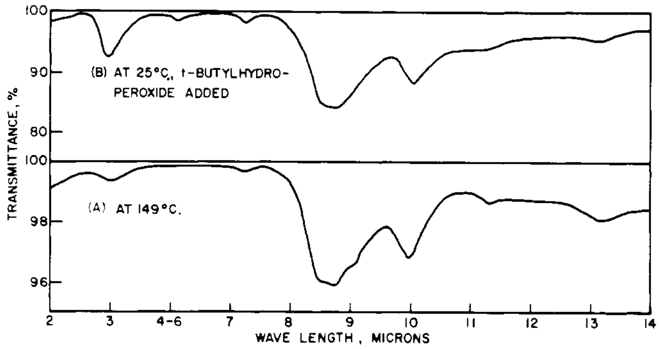


Figure 5. Spectra of films formed from cetane solutions of $Zn[PS_2(OC_3H_7)_2]_2$

The material responsible for the 8.7-micron infrared band is removed, if the mirror with film is rinsed in water. If, however, the mirror is wet with a few drops of barium chloride solution and then rinsed in distilled water, the material is not removed, as shown in part *B* (Figure 6). The spectrum is altered by barium chloride treatment and shows three sharp bands at 8.4, 8.9, and 9.25 microns. The material responsible for these three bands is removed by rinsing with hot, dilute sodium hydroxide solution. This chemical behavior as well as the spectral region of the absorption band (5) suggested that the infrared absorption band might be due to sulfate ions. This possibility was confirmed by treating a film of zinc sulfate with a few drops of barium chloride solution with the results shown in part *A* (Figure 6). Thus both spectra and chemical behavior indicate that sulfate ion is one of the components of the films whose spectra are shown in Figure 5.

Electron diffraction studies provided additional proof for the presence of sulfate ions. Attempts to identify components of the original films were not successful; no electron diffraction patterns were obtained. However, films treated with barium chloride solution and rinsed in water gave electron diffraction patterns characteristic of barium sulfate.

The question of the cation associated with the sulfate anion had not been answered conclusively. There can be little doubt it is Zn^{+2}. X-ray fluorescence shows that zinc is present in these films and that when the 8.7-micron band is removed, there is a decrease in the zinc content of the films. It was also demonstrated in one experiment that $ZnSO_4$ is produced under the conditions used to form these films. Silver mirrors were heated in a white oil solution of neutral *Z* for 30 minutes at 121° C. A sulfate-containing film was produced on the mirrors. A few milligrams of a white precipitate was filtered out of the oil. X-ray diffraction analysis of this precipitate showed $ZnSO_4 \cdot 6H_2O$ as the main consitutent and $ZnSO_4 \cdot H_2O$ as a minor constituent.

To try to determine if there were other components of the film in addition to sulfate, films were prepared on silver mirrors and rinsed in a variety of solvents. It was found that the bands due to adsorbed *Z* were removed by rinsing in boiling acetone just as found previously for the films containing zinc oxide. Rinsing with methanol removed the absorption in the 8.7-micron region and left a broad band in the 9- to 10-micron region as illustrated in Figure 7. The 3.0-micron band was not removed by the methanol rinse and therefore must be associated with the material

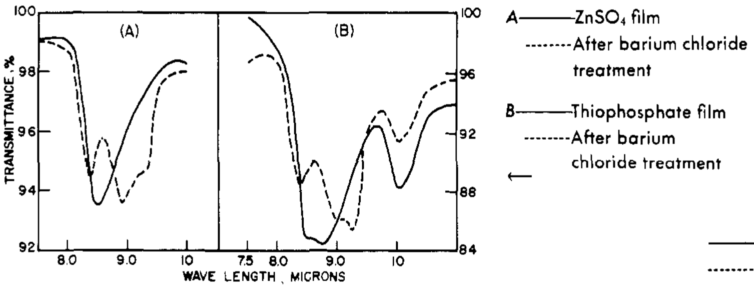


Figure 6. Effect of barium chloride treatment on film spectra

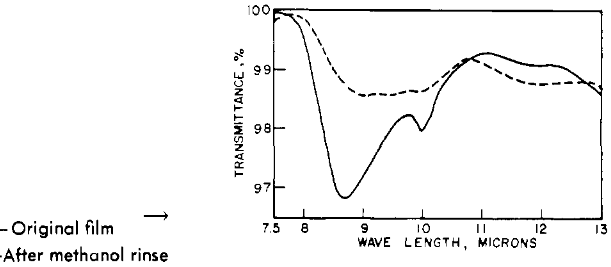


Figure 7. Effect of methanol rinse on film formed at 149° C. from cetane solution of neutral zinc additive

absorbing in the 9 to 10-micron region. Films washed with methanol did not give a positive test for sulfate ions, indicating again that the 8.7-micron band is associated with sulfate ions in the films. The methanol rinse removed less than half of the total zinc in the films. A water rinse removed the material giving the broad band in the 9 to 10-micron region, that giving the 3-micron band, and also nearly all the zinc remaining in the film.

These results with different solvents indicate that the zinc in the original film is divided among at least three components. Two of these components are identified as sulfate, probably $ZnSO_4$, and adsorbed neutral Z. However, more than one half of the zinc content of the film remains after these two components are removed. There must be one or more additional zinc compounds remaining on the surface after the methanol rinse. From the position of the absorption, 9 to 10 microns, and the knowledge that the film was produced from a thiophosphate, it is extremely probable that the material is a zinc thiophosphate of some sort. However, the possible structures of these types of materials are so numerous that there is little likeihood of identifying any specific compound from the infrared spectrum alone.

Films Formed by Rubbing. Figure 8 shows the spectrum of the benzene-insoluble material produced on a silver mirror by rubbing zinc diisobutyldithiphosphate on the surface with degreased cotton batting. This decomposition product, characterized by a single sharp band at 9.6 microns, was obtained on nickel, copper, silver, steel, and aluminum mirrors and from zinc additives in which the alkyl group was isopropyl, isobutyl, and isohexyl. This decomposition product has not been identified with certainty. The spectral position of the absorption band and the fact that only one band is observed (*5*) suggest that the material contains the PO_4^{-3} ion. Less symmetrical structures would be expected to have more than one band. Films of orthophosphoric acid have their strongest band at 9.6 microns. Furthermore, the spectral changes produced by heating are similar for H_3PO_4 and for this decomposition product. The material may be H_3PO_4 or a metal phosphate; further work is required to prove its identity.

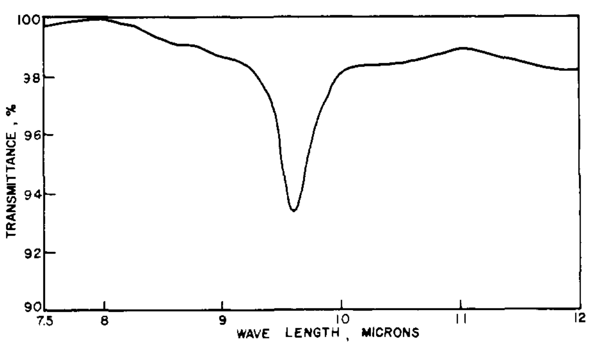


Figure 8. Film produced by rubbing zinc diisobutyl dithiophosphate on silver mirrors

GENERAL DISCUSSION

At least five components have been observed in the films produced by decomposition of zinc dialkyl dithiophosphates on metal surfaces. Three of these have been identified as sulfate (probably zinc sulfate), zinc oxide, and adsorbed molecules of the zinc additive. Spectra have been observed of at least two other decomposition products. One is formed under oxidizing conditions and is a zinc-containing material characterized by bands at 3.0 microns and in the 9 to 10-micron region. The other is produced by rubbing and is characterized by a band at 9.6 microns.

It seems reasonable to associate the zinc additive's ability to decompose peroxides, and thereby reduce oxidation, with the sulfate formation observed in these studies. Thus, either the presence of hydroperoxide or solution temperatures in the range where hydrocarbon oxidation would be expected resulted in sulfate formation. The results strongly suggest that sulfate is produced by oxidation of sulfur in the zinc additive to sulfate in the presence of peroxides and hydroperoxides.

The question of what material is responsible for reducing wear and preventing scuff is still unanswered. The material characterized by the 9.6 micron band or the material characterized by the broad 9 to 10 micron band appear to be the more likely possibilities. Of course, it is also possible that the antiwear material has not been observed at all in these experiments.

It is evident that this work has led to only a partial understanding of the reactions of zinc dialkyl dithiophosphates at metal surfaces. It has provided an identification of some of the compounds which are formed, and it has demonstrated many of the experimental variables which are important in these reactions. It has also demonstrated the complexity of the reactions which this type of material can undergo. It seems likely that further progress in understanding these reactions will be most rapid if the infrared and radioactive tracer techniques are employed simultaneously.

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