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ESR Studies of Carboxylic Acid- and Ester-Radical Anions Produced by γ-Irradiation at 77°K

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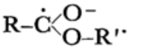
A series of monocarboxylic acids and esters have been γ-irradiated at 77°K, either pure or in the rigid matrix of 2-methyltetrahydrofuran, and the products have been examined by ESR spectroscopy. The spectra obtained in the pure state showed that the primary paramagnetic species in each case is the corresponding radical anion,  $\mathrm{R{-}\dot{C}}\left\langle\begin{matrix}\mathrm{O^-}\\ \mathrm{O{-}R'}\end{matrix}\right.$. In the rigid matrix, these characteristic spectra have been obtained after illuminating the γ-irradiated sample with visible light at the expense of the spectra of trapped electrons. When ultraviolet light was used for the illumination, the spectra of the radical anions disappeared, but instead appeared the spectra of the radicals produced by the decomposition of the radical anions. The latter spectra were almost the same as those obtained by the direct photolyses of acids and esters.

Many radicals and ions in rigid matrices at low temperatures have been characterized by their optical and ESR spectra.[1-4] These unstable intermediates are usually produced by the irradiation of ultraviolet light or γ-rays. As the rigid matrix, 2-methyltetrahydrofuran (MTHF) has often been used; in it trapped electrons are easily formed by γ-irradiation. When electrophilic molecules are present in the matrix, electrons released from the traps by the illumination of visible light are captured by the solute molecules. In the present paper, a series of monocarboxylic acids and esters are used as the solutes.

In 1959, Alger, Anderson and Webb[5] examined X-irradiated formic and acetic acids and several esters of these acids by ESR spectroscopy; they observed doublet spectra in every case, but they did not assign the spectra. Miyagawa and Gordy[6] also studied X-irradiated acetic acid and discussed the paramagnetic species responsible for the doublet spectrum.

In connection with a study of the behavior of electrons in rigid matrices, we reinvestigated the radiolyses and the photolyses of carboxylic acids and esters, both pure and in the matrix of MTHF, by means of ESR spectroscopy. While the present research was being undertaken, a study[7] appeared on a series of carboxylic acid radical anions, where the anions were prepared by the reaction with alkali metals. Our results on the acids are almost entirely consistent with theirs, but quantitatively a few variances are observed.

Experimental

Commercially-available carboxylic esters, methyl formate, methyl acetate, ethyl acetate, propyl acetate, methyl propionate, ethyl propionate, methyl *n*-butyrate, and methyl pivalate were purified by trap-to-trap distillations. Formic acid, acetic acid, propionic acid, and fully-deuterated acetic acid commercially obtained were used without purification. MTHF was stored in a sodium mirror for more than a day before use. For irradiating samples, carboxylic acids, esters, and MTHF containing small amounts of esters were frozen in Spectrosil tubes at the temperature of liquid nitrogen. These tubes were irradiated at 77°K with ^{60}Co γ-rays for half an hour at the dose rate of 2.2×10^5 R/hr. After the irradiation, samples were examined in the dark by means of a JEP-1 X-band ESR spectrometer with a field modulation of 100 kc/sec. After the initial measurement, bleaching experiments were performed with visible light from a tungsten lamp, and then with ultraviolet light from a Toshiba SHL-100 UV-2 mercury lamp. On the other hand, direct photolyses of several esters with ultraviolet light were also performed. As the standard for determining the hyperfine splitting constants and the line widths observed, $\mathrm{Mn^{2+}}$ in MgO was applied to the cavity.

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[1] G. N. Lewis and D. Lipkin, *J. Am. Chem. Soc.*, **83**, 1036 (1961).

[2] M. K. Carter and G. Vincow, *J. Chem. Phys.*, **47**, 292 (1967).

[3] T. Shida and W. H. Hamill, *J. Am. Chem. Soc.*, **88**, 3683 (1966).

[4] T. Shida and W. H. Hamill, *J. Chem. Phys.*, **44**, 2369 (1966).

[5] R. S. Alger, T. H. Anderson and L. A. Webb, *ibid.*, **30**, 695 (1959).

[6] I. Miyagawa and W. Gordy, *J. Am. Chem. Soc.*, **83**, 1036 (1961).

[7] J. E. Bennett and L. H. Gale, *Trans. Faraday Soc.*, **64**, 1174 (1968).

Results

γ-Radiolyses of Pure Carboxylic Esters. An ESR spectrum of γ-irradiated ethyl acetate is shown in Fig. 1. The spectrum A was obtained immediately after γ-irradiation. This spectrum was little affected by the illumination of visible light, while 2 min illumination with ultraviolet light was enough to eliminate this characteristic spectrum of the doublet and produce instead a quartet due to methyl radicals, as is shown in the spectrum B of Fig. 1. The underlying weak spectra in the A and B consist of five lines which are probably due to the radical, $CH_3COO\dot{C}HCH_3$.[8,9] Characteristic doublet spectra obtained with γ-irradiated ethyl acetate were also observed with other esters, such as methyl acetate, propyl acetate, methyl propionate, ethyl propionate, and methyl *n*-butyrate. As an example, the ESR spectrum of γ-irradiated propyl acetate is

TABLE 1. MAIN ESR SPECTRUM OF γ-IRRADIATED MONOCARBOXYLIC ESTERS AND ACIDS

Compound	No. of line	Hfs const. (oe)	Line widths (oe)
$HCOOCH_3$	1	—	6.3
CH_3COOCH_3	2	$23._3$	4.3
$CH_3COOC_2H_5$	2	$23._3$	6.1
$CH_3COOC_3H_7$	2	$21._5$	7.3
$C_2H_5COOCH_3$	2	$20._7$	6.4
$C_2H_5COOC_2H_5$	2	$21._5$	7.3
$C_3H_7COOCH_3$	2	$21._5$	6.4
$(CH_3)_3CCOOCH_3$	1	—	$10._3$
$HCOOH$	2	$12._7$	9.0
CH_3COOH	2	$34._1$	$12._5$
CD_3COOD	3	5	2.5
C_2H_5COOH	2	$26._7$	$12._7$

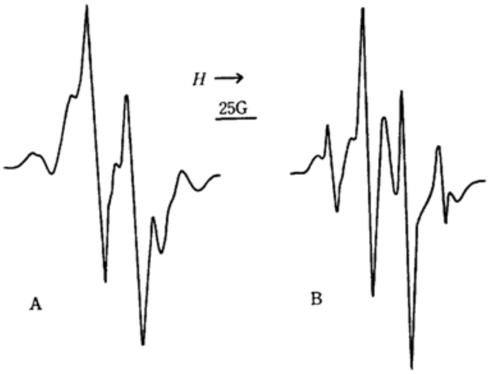

Fig. 1. ESR spectra of γ-irradiated ethyl acetate.
A: immediately after γ-irradiation
B: after bleaching by UV light

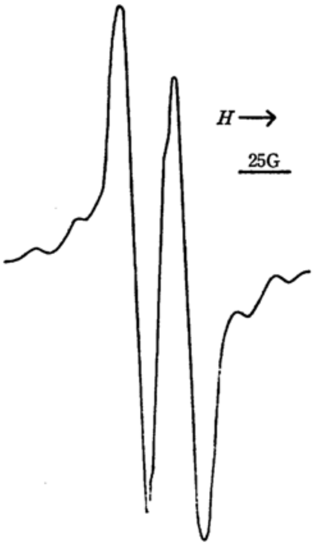

Fig. 2. ESR spectrum of γ-irradiated propyl acetate.

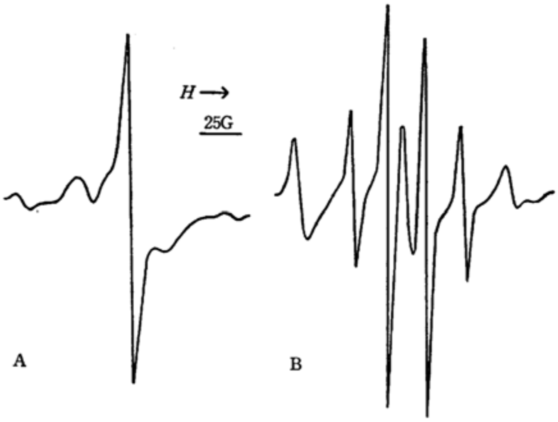

Fig. 3. ESR spectra of γ-irradiated methyl formate.
A: immediately after γ-irradiation
B: after bleaching by UV light

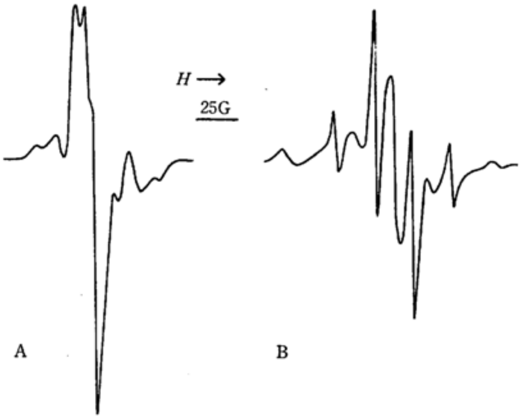

Fig. 4. ESR spectra of γ-irradiated methyl pivalate.
A: immediately after γ-irradiation
B: after bleaching by UV light

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8) H. Zelde and R. Livingston, *J. Chem. Phys.*, **30**, 40 (1959).

9) W. A. Seddon and D. R. Smith, *Advan. Chem. Ser.*, **82**, 163 (1968).

shown in Fig. 2. All these doublet spectra were little affected by the visible light-illumination, but were converted to the spectra due to such radicals as methyl and formyl by the ultraviolet light-illumination. The underlying spectra for each ester were well explained as being due to the following radicals: $CH_3COO\dot{C}H_2$ or $\dot{C}H_2COOCH_3$ for methyl acetate, $CH_3COOCH_2\dot{C}HCH_3$ for propyl acetate, $CH_3\dot{C}HCOOCH_3$ for methyl propionate, and $CH_3\dot{C}HCH_2COOCH_3$ for methyl butyrate. Table 1 summarizes the hyperfine splitting constants and the line-widths of the doublets, including the results obtained with methyl formate, methyl pivalate, and several carboxylic acids. The ESR spectrum of γ-irradiated methyl formate is shown in Fig. 3. A strong singlet spectrum is seen at the center. This singlet was not affected by the visible light-illumination, but upon ultraviolet illumination for 2 min it changed to the spectra mainly due to methyl radicals. The underlying spectra in the A of Fig. 3 are probably due to $HCOO\dot{C}H_2$ and $\dot{C}HO$. These spectra became stronger after the ultraviolet illumination. Figure 4 shows the ESR spectrum of γ-irradiated methyl pivalate. The underlying spectra are probably due to the radicals, $\dot{C}H_3$ and $(CH_3)_2\dot{C}H_2CCOOCH_3$ or $(CH_3)_3CCOO\dot{C}H_2$. The singlet spectrum at the center decayed a little upon the visible light-illumination. Upon the ultraviolet illumination, however, it immediately changed to the spectra due to methyl and formyl radicals, as is shown in Fig. 4.

We also made observations with monocarboxylic acids under the same condition as for their esters. The results are included in Table 1. These characteristic spectra were almost the same as those already reported by Bennett and Gale using alkali metal-deposition on the acids in preparing the paramagnetic species.7) The coincidence in the splitting constants and in the line-widths of the spectra is satisfactory.

Ultraviolet Photolyses of Esters. Most of the esters, when frozen at 77°K, become polycrystalline; this is not desirable for the photolyses. Therefore, the experiments were performed with only the five esters which become glassy or nearly glassy at 77°K. These samples were irradiated for about half an hour with a high-pressure mercury lamp. In the case of methyl formate, the spectra due to three radicals, $\dot{C}H_3$, $\dot{C}HO$, and $HCOO\dot{C}H_2$, were observed. Similar spectra were obtained with methyl acetate, and it was noticed that the spectrum due to methyl radicals decayed more rapidly in methyl formate than in methyl acetate at the temperature of liquid nitrogen. Figure 5 shows the ESR spectrum of UV-irradiated ethyl acetate. The spectrum may be identified as being due to the two radicals, $\dot{C}H_3$ and $\dot{C}H_3COOCHCH_3$. The spectra obtained with other esters, methyl acetate, ethyl propionate, and methyl pivalate, were also well explained by the combination of those due to $\dot{C}H_3$ and $\dot{C}HO$ radicals and the radicals produced by the cleavage at the weakest C–H bond of esters. With ethyl propionate, the contribution of the formyl radical was extremely small and the spectrum due to ethyl radicals was observed instead of that due to methyl radicals.

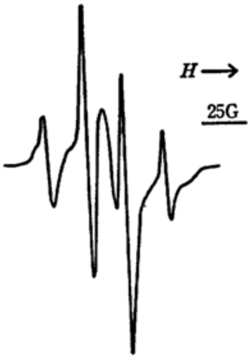

Fig. 5. ESR spectrum of UV-irradiated ethyl acetate.

As has been stated above, ultraviolet irradiation does not give the characteristic spectra obtained by γ-irradiation, such as the doublet with methyl acetate and the singlet with methyl pivalate.

γ-Radiolyses of Esters in the Rigid Matrix of MTHF. The ESR spectrum observed immediately after the γ-irradiation of pure MTHF consisted of a large singlet and a small seven-line spectrum. The singlet may be due to trapped electrons, while the underlying spectrum is probably due to MTHF radicals.10) When a small quantity of a solute such as a carboxylic ester or sulfur hexafluoride was added to the matrix, the singlet spectrum was reduced. In Fig. 6, the peak height of the singlet

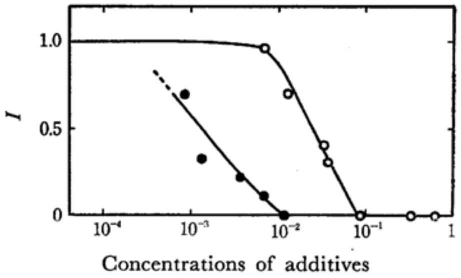

Fig. 6. Relative peak heights (I) of the spectra due to trapped electrons in γ-irradiated MTHF as a function of the mole fractions of additives.
○: ethyl acetate
●: sulfur hexafluoride

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10) D. R. Smith and J. J. Pieroni, *Can. J. Chem.*, **43**, 876 (1965).

is plotted as a function of the concentrations of sulfur hexafluoride and ethyl acetate. In the present experiment, the concentration of esters in the matrix was always kept within the range of 1 to 2 mol%, so that the peak height of the singlet obtained immediately after γ-irradiation was almost the same as that obtained with pure MTHF. After the illumination with visible light, however, spectra characteristic of γ-irradiated pure esters appeared at the expense of this singlet spectrum. Figure 7 shows the spectra obtained with γ-irradiated MTHF containing 1 mol% ethyl acetate before and after the illumination with visible light. Solute molecules with which the characteristic doublet was observed were methyl, ethyl and propyl acetate, ethyl and methyl propionate, and methyl butyrate. When ultraviolet light was used for the illumination, all the doublets disappeared and the spectra of such radicals as methyl and formyl appeared. These changes correspond exactly to those observed in the pure states previously described. The hyperfine splitting constants and the line-widths of the doublets are summarized in Table 2.

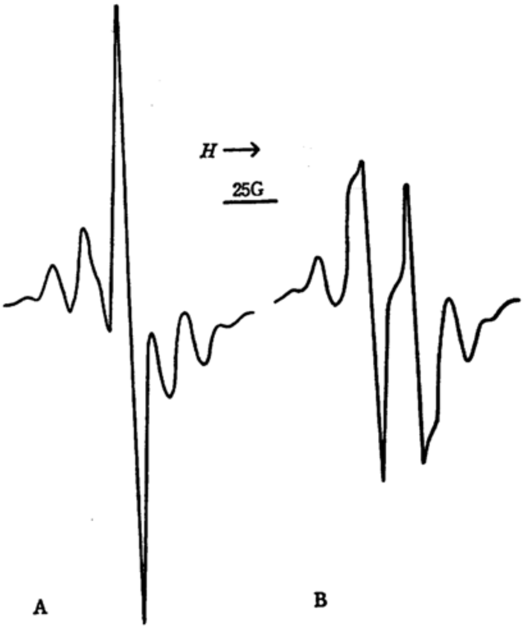


Fig. 7. ESR spectra of γ-irradiated MTHF containing 1 mol% ethyl acetate.
A: immediately after γ-irradiation
B: after bleaching by visible light

Acetic acid and propionic acid were also used for the solute molecules in the γ-irradiated MTHF glasses. The observed spectra correspond well to those obtained in the pure states. Fully-deuterated acetic acid was also examined. Judging from the spectrum obtained with the pure acid, the expected spectrum was a triplet with a hyperfine splitting constant of 5 G. However, the spectrum actually obtained was a broad singlet. This may be due to the overlap of the spectra due to various radicals produced by γ-irradiation. A similar result was obtained with formic acid; in the pure state a doublet

TABLE 2. MAIN ESR SPECTRUM OF γ-IRRADIATED MTHF CONTAINING MONOCABOXYLIC ESTERS OR ACIDS AFTER BLEACHING BY VISIBLE LIGHTS

Compound	No. of line	Hfs const. (oe)	Line widths (oe)
$HCOOCH_3$	1	—	6.7
CH_3COOCH_3	2	$23._6$	5.7
$CH_3COOC_2H_5$	2	$23._1$	7.6
$CH_3COOC_3H_7$	2	$23._0$	6.1
$C_2H_5COOCH_3$	2	$19._8$	5.3
$C_2H_5COOC_2H_5$	2	$21._2$	5.2
$C_3H_7COOCH_3$	2	$20._0$	5.5
$(CH_3)_3CCOOCH_3$	1	—	8.3
HCOOH	1	—	7.6
CH_3COOH	2	$32._0$	$10._3$
C_2H_5COOH	2	$25._4$	9.9
CD_3COOD	1	—	$12._5$

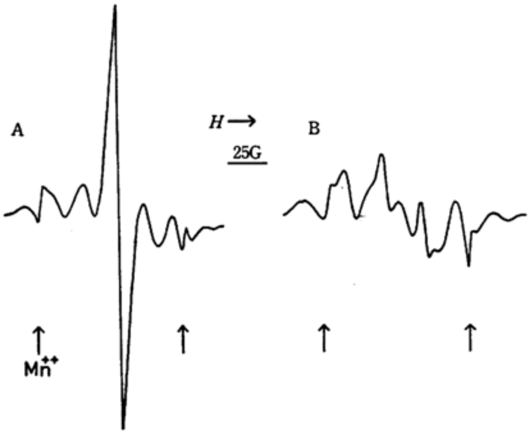


Fig. 8. ESR spectra of γ-irradiated MTHF containing 1 mol% methyl pivalate.
A: after bleaching by visible light
B: after bleaching by UV light

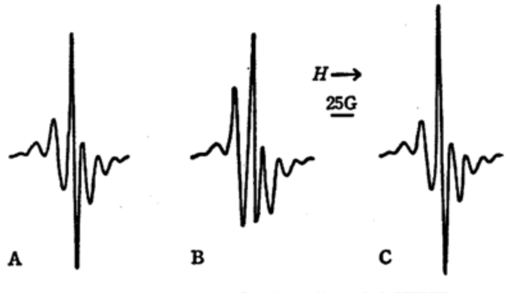


Fig. 9. ESR spectra of γ-irradiated MTHF containing 1 mol% methyl formate.
A: immediately after γ-irradiation
B: after 1-min illumination of visible light
C: after 3-min illumination of visible light

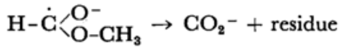
was obtained, but in the matrix a broad singlet was obtained. The spectra A and B in Fig. 8 show the ESR spectra obtained with γ-irradiated methyl pivalate-MTHF glass after the illumination with visible and ultraviolet light. The change from the spectrum A to B exactly corresponds to that observed in the pure state. Figure 9 shows the change in the spectrum obtained with a MTHF glass containing methyl formate during the illumination with visible light. At the beginning of the illumination, the singlet at the center decayed and a doublet appeared, but upon the continuous illumination the doublet diminished and the singlet increased again. The decreased singlet may be attributed to trapped electrons, but the cause of the increased one cannot be specified. This singlet may be the spectrum observed in the pure state. After the ultraviolet illumination, the singlet disappeared, leaving the spectra mainly due to methyl and formyl radicals.

Discussion

As may be seen in Tables 1 and 2, the spectra obtained with γ-irradiated pure carboxylic esters and acids are in good agreement with those obtained with γ-irradiated MTHF containing the corresponding esters and acids after the illumination with visible light. It is now well known that the singlet spectrum observed immediately after the γ-irradiation of a MTHF rigid glass is due to electrons trapped in the solvent and that this singlet is easily quenched by the illumination with visible light. Therefore, the spectra obtained with MTHF glass solutions after illumination with visible light are probably due to the paramagnetic species formed in the reaction of electrons with solute molecules.[3,4] Since carboxylic compounds have large electron affinities, the paramagnetic species above stated might be the corresponding radical anions. Bennett and Gale, using the technique of alkali metal deposition on the carboxylic acids at the temperature of liquid nitrogen, observed the spectra due to the products. The spectra they observed with acids are very similar to those we obtained with acids and esters. They assigned these spectra to the corresponding radical anions, $\mathrm{R{-}\dot{C}}\langle{}^{\mathrm{O^-}}_{\mathrm{O{-}R'}}$. This assignment exactly fits the present results, except for the case of methyl formate.

If radical anions, $\mathrm{R{-}\dot{C}}\langle{}^{\mathrm{O^-}}_{\mathrm{O{-}R'}}$, are responsible for the characteristic spectra obtained with γ-irradiated esters, the doublets observed with esters having β-protons in the substitute, R, suggest that the bond $\mathrm{R{-}\dot{C}}$ does not rotate freely at the temperature of liquid nitrogen. This has already been substantiated in the case of acetic acid by Bennett and Gale; when the sample was warmed up from the temperature of liquid nitrogen, the doublet observed at 77°K was converted to a quartet typical of that observed in a freely-rotating methyl group, while the reverse process occurred when it was cooled again at 77°K. In the case of methyl pivalate, the corresponding characteristic spectrum observed was a singlet. This is consistent with the above assignment, because this ester has no β-protons.

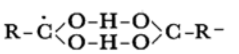
If the foregoing discussion is applicable to every acid and ester, formic acid and its esters should give a doublet spectrum because of the interaction of an α-proton. Bennett and Gale reported that they observed a doublet with methyl formate, although the details were not presented. As has been stated in the Results section, we observed a singlet with γ-irradiated methyl formate and a peculiar change in the spectrum with the MTHF rigid solution during the illumination with visible light, as is shown in Fig. 9. This change can tentatively be explained as follows; the decrease in the singlet by the illumination is due to the quenching of trapped electrons, while the increase in the doublet may be due to the formation of the radical anions, $\mathrm{H{-}\dot{C}}\langle{}^{\mathrm{O^-}}_{\mathrm{O{-}CH_3}}$. However, if this radical anion is unstable when illuminated with visible light, the following reaction may occur:



$$\mathrm{H{-}\dot{C}}\langle{}^{\mathrm{O^-}}_{\mathrm{O{-}CH_3}} \rightarrow \mathrm{CO_2^-} + \text{residue} \qquad (1)$$

In the present interpretation, this reaction corresponds to the change from the spectra B to the C in Fig. 9. Carbon dioxide anions are known to show a singlet and to be stable in visible light.[11] Accordingly, the singlet observed with γ-irradiated methyl formate may be explained in terms of the reaction (1) under γ-irradiation.

In the experiments of Bennett and Gale, carboxylic acids were examined mainly. Therefore, the paramagnetic species they obtained were perhaps dimer anions but were not the monomer radical anions:



$$\mathrm{R{-}\dot{C}}\langle{}^{\mathrm{O{-}H{-}O}}_{\mathrm{O{-}H{-}O}}\rangle\mathrm{C{-}R^-}$$

This consideration can also be applied to the present results obtained with acids. In the case of esters, however, the hydrogen bonding is not expected to be so strong that the characteristic spectra observed may be attributed to the monomer radical anions. This may explain the differences in the hyperfine splitting constants of acids and the corresponding esters.

The authors are indebted to Dr. K. Shimokoshi of this Institute for his valuable suggestion.

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[11] M. Shirom, R. F. C. Claridge and J. E. Willard, *J. Chem. Phys.*, **47**, 286 (1967).