

Addition of Thioglycolic Acid to α -Alkenes

BENGT SMITH and SVEN HERNESTAM

Institutionen för Organisk Kemi, Chalmers Tekniska Högskola, Göteborg, Sweden

In a recent study¹ one of us made use of the addition of thioglycolic acid to the ethylenic linkage in order to characterize the unsaturated hydrocarbons in a peat-tar fraction. It was found that alkenes, among other compounds, were present. Their structure was not definitely established, but the occurrence of normal α -alkenes was indicated.

To make a closer examination of this structural problem possible, it was decided to study in some detail the addition of thioglycolic acid to some α -alkenes in the range from octene to undecene. Holmberg² has studied the reaction between styrene and thioglycolic acid and Kharasch *et al.*³ the reaction between styrene or *isobutylene* and thioglycolic acid. Cunneen⁴ added thioglycolic acid to *cyclohexene* and 1-methyl*cyclohexene* whilst Hellström and Sandström⁵ added the same acid to some methyl*cyclohexenes*. Apart from an attempt by Hoog and Eichwald⁶ to isolate some alkenes from mixtures containing saturated hydrocarbons by means of thioglycolic acid, no investigation of the reaction between this reagent and long chain alkenes has been reported, according to our knowledge.

THE ADDITION REACTION

Thioglycolic acid is not miscible at room temperature with the alkenes from C₈ to C₁₁, and no reaction is observed when thioglycolic acid is dropped into an equimolecular amount* of the alkene. Vigorous shaking, however, rapidly brings about a violent reaction, the temperature rising to 50—60°. A typical yield-time curve is shown in Fig. 1. After about 2 minutes the yield of octylthioglycolic acid is 80 % and after half an hour 90 %. A final value of 95—97 % is reached in about 20 hours. The yield-time curve for the reaction between equimolecular amounts of thioglycolic acid and styrene** is also shown in Fig. 1. It is not possible to draw, from the shape of these curves, any definite conclusions concerning the relative reactivities of the above mentioned alkenes and styrene towards thioglycolic acid, as several factors influence the reaction (see below).

* Equimolecular amounts of alkene and thioglycolic acid were used throughout this work.

** Constructed from the values given by Holmberg².

Effect of peroxides and oxygen. It seems to be well established that the "abnormal" addition (see p. 1114) of thiols to unsaturated compounds is a chain reaction, proceeding through a radical mechanism^{3,7}. Consequently peroxides, present either as olefine peroxides or specially added, and also oxygen are of importance in the reaction. Cunneen⁴, for example, reported that cyclohexene and 1-methylcyclohexene, both freshly distilled in an atmosphere of nitrogen, did not react with thioglycolic acid at room temperature. Addition of a little ascaridole, however, caused an immediate reaction. Several attempts in this work to prevent the reaction between alkenes and thioglycolic acid by exclusion of peroxides and oxygen failed. In one case octene-1 was shaken with acid ferrous sulfate solution and then distilled over sodium in an atmosphere of oxygen-free nitrogen. The thioglycolic acid used was also distilled in an atmosphere of oxygen-free nitrogen and the mixing of the reagents carried out with the exclusion of oxygen. Nevertheless an immediate reaction ensued and the yield of octylthioglycolic acid was over 90 %. Hence only minute traces of oxygen seem to be necessary to catalyze the reaction.

Effect of antioxidants. In view of these results it was of interest to study the influence of antioxidants on the reaction between alkenes and thioglycolic acid. Addition of as little as 0.1 mol.-% of hydroquinone had a distinct effect. Only after about 20 minutes shaking did the reaction mixture become homogeneous, whilst in the absence of hydroquinone about 10 seconds were sufficient. The yield after 30 minutes was about 40 %, after 20 hours about 80 %. The temperature rose only a few degrees, compared to 30—40° in the absence of hydroquinone. When 0.5 mol.-% of hydroquinone was used, the reaction mixture was nonhomogeneous even after shaking for 48 hours and the yield was 8 %. These experiments demonstrate the retarding effect of antioxidants on the reaction between alkenes and thioglycolic acid.

Effect of ultraviolet light. The majority of the experiments in this work was performed in diffuse daylight. However, the reaction between alkenes and thioglycolic acid proceeded as readily in total darkness. Thus no irradiation with ultraviolet light is necessary under ordinary conditions.

Effect of impurities in the thioglycolic acid. Thioglycolic acid is generally prepared from chloroacetic acid and sodium or potassium hydrosulfide. The boiling points of thioglycolic acid and chloroacetic acid are close and repeated fractionation is necessary to obtain a pure product which nevertheless may still contain small amounts of chloroacetic acid. The possibility of this impurity on storage of the product, giving rise to some thiodiglycolic acid, $S(CH_2COOH)_2$, must be taken in account.

However, the principal change resulting from the storage of thioglycolic acid in contact with air is the formation of dithiodiglycolic acid, $HOOCCH_2SSCH_2COOH$. It has been stated⁶ that thioglycolic acid loses its activity on storage in contact with air, so some experiments were carried out to study the influence of dithiodiglycolic acid on the reactivity of thioglycolic acid towards alkenes.

Table 1 lists some semi-quantitative experiments with various specimens of thioglycolic acid and alkenes. For each experiment, this table shows the time elapsed from the mixing of the reagents (equimolecular amounts) and commencement of the shaking until the reaction mixture is homogeneous. Several experiments were made with each pair and the shortest time taken.

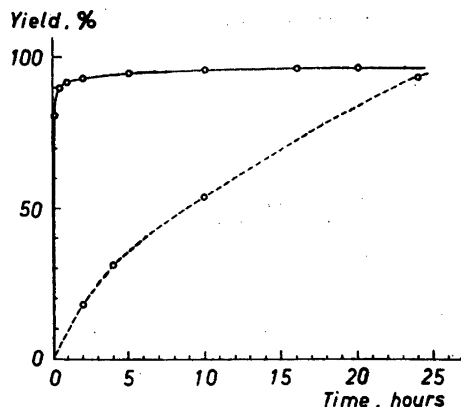


Figure 1. Yield-time curve for octene-1 and thioglycolic acid (—) and styrene and thioglycolic acid (---).

The decreasing reactivity of thioglycolic acid towards alkenes on storage is clearly demonstrated (Nos. 1—4). While the reaction time in the case of octene and nonene is only slightly increased, there is a marked difference in reactivity of freshly distilled and stored thioglycolic acid towards decene and 4-methyldecene and especially towards undecene. By addition of benzoyl peroxide to the pair, undecene and thioglycolic acid stored for 8 months, the reaction time was decreased from more than 60 minutes to 8 minutes.

In the experiments Nos. 5—8, various amounts of dithiodiglycolic acid were added to samples of freshly distilled thioglycolic acid and the effect on the reactivity of the latter noted. Comparison of the reaction times observed in these experiments with those in Nos. 1—4 indicates that the formation of dithiodiglycolic acid is not alone responsible for the decrease in reactivity of thioglycolic acid on storage as was assumed by Hoog and Eichwald⁶.

From experiments Nos. 9 and 10 with thioglycolic acid containing 1 % of chloroacetic acid and 1 % of thiodiglycolic acid, respectively, it appears that the small amounts of these compounds which may be present in "pure" thioglycolic acid do not affect its reactivity greatly.

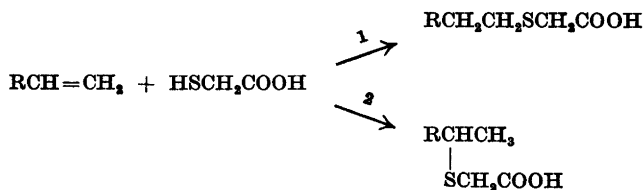
It is evident from the foregoing that thioglycolic acid, when stored in tightly stoppered bottles in contact with air (as was the case here) does not rapidly lose its reactivity towards alkenes. Even after 2 months it was as reactive as a freshly distilled sample.

Effect of impurities in the alkenes. The alkenes used were prepared by two methods, either from the appropriate alkyl magnesium bromides and allyl bromide or by pyrolysis of alkyl acetates. When the alkenes formed were carefully purified by prolonged boiling with metallic sodium and fractionation on an efficient column, there did not exist any difference in reactivity between specimens obtained by the two methods. However, in some cases, when using samples obtained by the allyl bromide method, the reaction did not start at all or gave low yields. It is possible that the presence of small amounts of impurities were responsible for this behaviour.

Table 1. Reactivity of thioglycolic acid towards alkenes as a function of time of storage and impurities.

| Experiment No. | Specimen of thioglycolic acid | Octene-1 | Nonene-1 | Decene-1 | 4-Methyl-decene-1 | Undecene-1 |
|----------------|-------------------------------------|----------|----------|----------------|-------------------|----------------|
| 1 | Freshly distilled (99.7 % purity) | 11 sec. | 10 sec. | 8 sec. | 20 sec. | 11 sec. |
| 2 | Stored for 2 months (99.4 % purity) | 7 sec. | 7 sec. | 9 sec. | 9 sec. | 18 sec. |
| 3 | Stored for 5 months (95.0 % purity) | 20 sec. | 26 sec. | 22 sec. | 27 sec. | 1 min. 43 sec. |
| 4 | Stored for 8 months (92.0 % purity) | 21 sec. | 25 sec. | 1 min. 12 sec. | 2 min. | >60 min. |
| 5 | With 1 % of dithiodi-glycolic acid | 11 sec. | 15 sec. | 16 sec. | 15 sec. | 32 sec. |
| 6 | With 2 % of dithiodi-glycolic acid | 13 sec. | 14 sec. | 18 sec. | 22 sec. | 33 sec. |
| 7 | With 5 % of dithiodi-glycolic acid | 12 sec. | 15 sec. | 16 sec. | 20 sec. | 50 sec. |
| 8 | With 10 % of dithiodi-glycolic acid | 12 sec. | 19 sec. | 26 sec. | 30 sec. | 2 min. 30 sec. |
| 9 | With 1 % of chloro-acetic acid | 11 sec. | 12 sec. | 15 sec. | 17 sec. | 30 sec. |
| 10 | With 1 % of thiodi-glycolic acid | 12 sec. | 14 sec. | 16 sec. | 25 sec. | 1 min. 9 sec. |

Structure of the addition products. The addition of thioglycolic acid to α -alkenes may result in the formation of two different products.



The reaction may proceed either contrary to Markownikoff's rule ("abnormal addition"), or according to this rule ("normal addition"). All alkenes investigated in this work reacted exclusively according to the former type of addition. In no instances could products formed by the reaction path 2 be traced. The structures of the alkylthioglycolic acids formed were established by comparison with the properties of alkylthioglycolic acids prepared from the appropriate alkyl bromides and sodium thioglycolate or with literature values (see Table 2).

Although the reaction between thiols and olefines is generally "abnormal", it has been possible to alter the addition in some instances by using catalysts such as sulfur or sulfuric acid^{9,10}. However, sulfur did not change the "abnormal" reaction between octene-1 and thioglycolic acid, *n*-octylthioglycolic acid being formed exclusively. When sulfuric acid is used as a catalyst the

Eqv. of bromine consumed per mole
of *n*-nonylthioglycolic acid

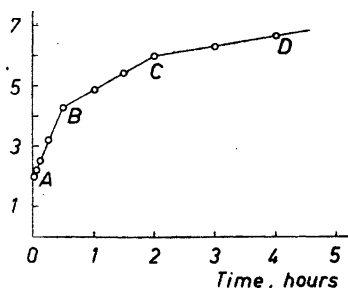


Figure 2. Diagram illustrating the reaction between *n*-nonylthioglycolic acid and bromine.

reaction is not to be considered as an addition of thiol to alkene. In this case sulfuric acid first adds to the double bond and the resulting ester subsequently reacts with the thiol¹⁰. As the addition of sulfuric acid to olefines proceeds according to Markownikoff's rule the reaction product between ester and thiol is the "normal" one. No experiments using sulfuric acid as a catalyst were made in this work.

Jones and Reid⁹ found that ethane thiol reacted with propylene giving ethyl-*n*-propyl sulfide in the presence of peroxides and ethyl-*i*-propyl sulfide in their absence. In the previously described experiment (p. 1112) where octene-1 was allowed to react with thioglycolic acid in the absence of peroxides and oxygen, only *n*-octylthioglycolic acid was formed. This was also the case in the presence of hydroquinone.

Alkylsulfinylacetic and alkylsulfonylacetic acids

In order to compare the properties of some pure alkylsulfonylacetic acids with those of the sulfonylacetic acids obtained in the above-mentioned investigation of the alkenes contained in a peat-tar fraction, the alkylthioglycolic acids were oxidized by potassium permanganate to the corresponding alkylsulfonylacetic acids.

The reaction of the alkylthioglycolic acids with bromine presented some interesting points. Fig. 2 demonstrates the course of the reaction between *n*-nonylthioglycolic acid and bromine in excess. Two equivalents of bromine are used up instantly with the formation of the sulfinylacetic acid and subsequently (stage A—B) the oxidation of the sulfinylacetic acid to sulfonylacetic acid takes place. Stage B—C obviously represents substitution of hydrogen by bromine, probably in the methylene group situated between the carboxyl and sulfonyl groups. Further substitution meets with greater resistance (stage C—D).

As a result of the rapid oxidation of the alkylthioglycolic acids in question to the corresponding sulfinylacetic acids, the method of Siggia and Edsberg¹¹ for the quantitative determination of alkyl sulfides gave good results (see

Table 2. Alkylthioglycolic acids $RSCH_2COOH$.

| R | B.p. °C (mm) | M.p. °C | % S | | Equiv.wt. a | | Equiv.wt. b | | Method of preparation c |
|-----------------------------------|----------------|---------|-------|--------|-------------|--------|-------------|--------|-------------------------|
| | | | Found | Calcd. | Found | Calcd. | Found | Calcd. | |
| $n-C_8H_{17}$ | 138 (0.35) | 36.9 d | 15.9 | 15.69 | 204.2 | 204.3 | 102.1 | 102.2 | A |
| $n-C_9H_{19}$ e | 137 (0.70) | < 0 f | 15.6 | 15.69 | 204.7 | 204.3 | 102.6 | 102.2 | B |
| $n-C_9H_{19}$ g | 157 (0.67) | 53.4 h | 14.6 | 14.68 | 218.6 | 218.4 | 109.1 | 109.2 | A |
| $n-C_{10}H_{21}$ | — | 51.8 i | 13.7 | 13.80 | 231.9 | 232.2 | 116.0 | 116.2 | A |
| $n-C_{11}H_{23}$ g | — | 63.0 j | 13.1 | 13.01 | 247.5 | 246.4 | 123.8 | 123.2 | A |
| 4- CH_3 - $n-C_{10}H_{21}$ g, k | 126—127 (0.02) | < 0 l | 13.2 | 13.01 | 244.0 | 246.4 | 123.0 | 123.2 | A |

a. Titration with 0.1 *N* sodium hydroxide against phenolphthalein.

b. " " 0.05 *N* bromide-bromate solution.

c. Method A means addition of thioglycolic acid to the corresponding α -alkene.

" B " reaction of an alkyl bromide with sodium thioglycolate.

d. Literature value 36—37° e.

e. $d_4^{20} = 0.9940$, $n_D^{20} = 1.4751$, $MR_D = 57.9$ (found) 57.87 (calcd.).

f. M. p. of benzyl thiuronium salt 137°.

g. New compound.

h. No depression of the m. p. on admixture with *n*-nonylthioglycolic acid prepared by method B, m. p. 53°.

i. Literature value 52—53° e.

j. No depression of the m. p. on admixture with *n*-undecylthioglycolic acid prepared by method B, m. p. 63°.

k. $d_4^{20} = 0.9703$, $n_D^{20} = 1.4753$, $MR_D = 71.5$ (found) 71.57 (calcd.).

l. M. p. of benzyl thiuronium salt 147°. M. p. of the thiuronium salt of 4-methyldecylthioglycolic acid prepared by method B, 146°. Mixed m. p. 146°.

Table 2). This method involves direct titration with 0.05 *N* bromide-bromate solution in an acidic medium.

The method was also found suitable for the preparation of alkylsulfinylacetic acids from alkylthioglycolic acids. For this purpose, however, a 0.5 *N* bromide-bromate solution was used. The physical constants and analyses for the sulfinylacetic and sulfonylacetic acids are given in Tables 3 and 4.

Table 3. Alkylsulfinylacetic acids $RSOCH_2COOH$ *.

| R | M.p. °C | % S | | Equiv.wt. ** | |
|------------------|-----------|-------|--------|--------------|--------|
| | | Found | Calcd. | Found | Calcd. |
| $n-C_8H_{17}$ | 60.4 | 14.5 | 14.55 | 221.0 | 220.3 |
| $n-C_9H_{19}$ | 70.3 | 13.6 | 13.68 | 234.7 | 234.4 |
| $n-C_{10}H_{21}$ | 74.9 | 12.7 | 12.91 | 249.0 | 248.4 |
| $n-C_{11}H_{23}$ | 81.1—81.5 | 12.3 | 12.22 | 261.0 | 262.4 |

* All compounds in this table are new.

** Titration with 0.1 *N* sodium hydroxide against phenolphthalein.

Table 4. Alkylsulfonylacetic acids RSO_2CH_2COOH .

| R | M.p. °C | % S | | Equiv.wt. ^a | |
|--|-------------|-------|--------|------------------------|--------|
| | | Found | Calcd. | Found | Calcd. |
| <i>n</i> -C ₈ H ₁₇ ^b | 96.5 | 13.5 | 13.57 | 236.9 | 236.3 |
| <i>s</i> -C ₈ H ₁₇ ^c | 16–17.5 | 13.2 | 13.57 | 233.3 | 236.3 |
| <i>n</i> -C ₉ H ₁₉ ^c | 105.1 | 12.7 | 12.81 | 249.8 | 250.4 |
| <i>n</i> -C ₁₀ H ₂₁ ^d | 105.7 | 12.0 | 12.13 | 264.7 | 264.4 |
| <i>n</i> -C ₁₁ H ₂₃ ^c | 111.0–111.6 | 11.5 | 11.52 | 278.0 | 278.4 |

a. Titration with 0.1 *N* sodium hydroxide against phenolphthalein.

b. Prepared previously by Newman *et al.* ¹², no m.p. reported.

c. New compound.

d. Literature value 104–105° ⁸.

Melting points of the acids

In the utilization of thioglycolic acid for the identification of alkenes, the melting points of the alkylthioglycolic, alkylsulfinylacetic, and alkylsulfonylacetic acids are of special interest. In Table 5 the melting points of some acids of these types, prepared in this work or taken from the literature, are compiled together with the melting points of the corresponding fatty acids, derived from the alkylthioglycolic acids by replacing the sulfur atom by a methylene group.

The melting points of the normal alkylthioglycolic acids increase as the series is ascended, but not regularly. The acids with an uneven number of carbon atoms in the alkyl group melt at higher temperatures than those which immediately follow them, and contain one carbon atom more. The normal alkylthioglycolic acids thus fall into two series as regards melting point, just as is the case with the normal fatty acids. In the series of normal alkylsulfinylacetic acids and normal alkylsulfonylacetic acids, however, irregularities exist. Replacement of a β -methylene group in a normal fatty acid by a sulfur atom raises the melting point by 9–11°.

Table 5. Melting points (°C) of some sulfur containing acids and the corresponding fatty acids.

| R | RSCH ₂ COOH | RSOCH ₂ COOH | RSO ₂ CH ₂ COOH | RCH ₂ CH ₂ COOH ^a |
|---|------------------------|-------------------------|---------------------------------------|--|
| <i>n</i> -C ₇ H ₁₅ | — | — | 95.5–96 ^b | 31.4 |
| <i>n</i> -C ₈ H ₁₇ | 36.9 | 60.4 | 96.5 | 28.0 |
| <i>n</i> -C ₉ H ₁₉ | 53.4 | 70.3 | 105.1 | 43.6 |
| <i>n</i> -C ₁₀ H ₂₁ | 51.8 | 74.9 | 105.7 | 40.5 |
| <i>n</i> -C ₁₁ H ₂₃ | 63.0 | 81.1–81.5 | 111.0–111.6 | 54.0 |
| <i>n</i> -C ₁₂ H ₂₅ | 61–62 ^c | — | 108–109 ^d | 52.1 |
| <i>s</i> -C ₈ H ₁₇ | < 0 | — | 16–17.5 | liquid ^e |
| 4-CH ₃ - <i>n</i> -C ₁₀ H ₂₁ | < 0 | — | — | — |

a. M. p. from ref. ¹³. b. Ref. ¹⁴. c. Ref. ⁸. d. Ref. ¹⁵. e. Ref. ¹⁶.

Branching of the chain causes the melting point to drop appreciably as demonstrated by the *s*-octylthioglycolic, *s*-octylsulfonylacetic, and 4-methyldecylthioglycolic acids. This fact is in accordance with the general rule that the melting point is raised by increasing the symmetry of the molecule. It is of value for the distinguishing of normal α -alkenes on one hand and α -alkenes with branched chain as well as alkenes with the double bond elsewhere than in the α -position on the other hand by means of thioglycolic acid.

For the identification of liquid alkylthioglycolic acids the benzyl thiuronium salts have proved very suitable.

EXPERIMENTAL

Alkenes

For the preparation of the alkenes two methods were utilized.

Method 1 involved the reaction of an alkyl magnesium bromide with allyl bromide in ether solution. After refluxing for one hour the reaction mixture was treated with water and then steam distilled. The organic layer was separated, dried and fractionated. The crude alkene was refluxed over sodium as long as any precipitate was formed and finally distilled using an efficient column. Using this method octene-1, nonene-1, and decene-1 were obtained as well as 4-methyldecene-1.

Method 2 involved the pyrolysis of alkyl esters of acetic acid at 500° C according to the procedure described by Geldof and Wibaut¹⁷. The crude alkenes were treated as above. Using this method octene-1, nonene-1, decene-1, and undecene-1 were obtained. The physical constants of the alkenes were in very good agreement with reliable literature values.

Alkylthioglycolic acids

Addition reactions. Equivalent amounts of alkene and thioglycolic acid were mixed and shaken. The reaction generally started immediately, the mixture becoming homogeneous and the temperature rising to 50–60°. After about half an hour the temperature had decreased to room temperature. The yield at this stage was about 90%. Higher yields (about 95%) could be obtained by warming the reaction mixture for another 15–20 hours to 50–60°. It was also possible to use glacial acetic acid or benzene as solvent, preferably the same volume as the volume of alkene. Too much solvent must be avoided. In this case the reaction mixture was homogeneous from the beginning. The reaction proceeded in much the same way as in the absence of solvent. After half an hour the reaction mixture had reached room temperature and the yield was about 85%. After a further period of 15–20 hours at room temperature the yield increased to about 93%.

In the addition reactions with octene-1, nonene-1, and 4-methyldecene-1, the solvent (if used) together with the alkene and thioglycolic acid not consumed were distilled from the reaction mixture and the remaining addition product then fractionated at low pressure. The alkylthioglycolic acid obtained was, if solid, recrystallized from ligroin to constant melting point.

In the addition reactions with decene-1 and undecene-1 the residue after removal of the low-boiling components was not distilled but directly recrystallized from ligroin.

Alkylthioglycolic acids from alkyl bromides and sodium thioglycolate were obtained according to Larsson¹⁸ and purified as described above.

Alkylsulfanylacetic and alkylsulfonylacetic acids

Alkylsulfanylacetic acids. The alkylthioglycolic acid (0.01 mole) was dissolved in 50 ml of glacial acetic acid, containing 3 ml of conc. hydrochloric acid, and 40.0 ml of a 0.5 *N* bromide-bromate solution was added dropwise. Pouring of the mixture into ice water produced crystals of the alkylsulfanylacetic acid. They were separated by filtration. Extraction of the filtrate with warm chloroform (35°) furnished some more of the sulfanyl-

acetic acid. Yield 85–95 %. The crude product was washed with warm petroleum ether only since the alkylsulfinylacetic acids were liable to decompose when dissolved in boiling solvents (*e. g.* benzene, ethyl acetate). The washing procedure, by which remaining alkylthioglycolic acids were removed, was repeated until a constant melting point was obtained. The alkylsulfinylacetic acids slowly decomposed on storage.

Alkylsulfonylacetic acids. The alkylthioglycolic acids were oxidized with potassium permanganate essentially as described by Holmberg². The yield of alkylsulfonylacetic acids was 90–100 %. The crude products were recrystallized from water to constant melting points.

SUMMARY

The addition of thioglycolic acid to some α -alkenes was studied under various conditions. The addition took place exclusively against Markownikoff's rule, with excellent yields of alkylthioglycolic acids.

Alkylsulfinylacetic and alkylsulfonylacetic acids were prepared from the alkylthioglycolic acids by oxidation with bromine and potassium permanganate, respectively.

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