high-speed emulsions the proportion of iodide is greater in the larger than in the smaller grains.[8] Further, it has been shown by Sheppard, Wightman and Trivelli[9] and by Clark[10] that the larger grains resist desensitizing more than the small ones. This may be due to the silver sulfide nuclei being larger or more firmly "rooted," and protected by silver iodide rather than silver bromide, in the larger grains.

Summary

1. The literature on the double compounds of thio-ureas with silver salts is briefly reviewed.

2. The preparation of the 1:1 compounds of allylthio-urea with silver chloride, silver bromide and silver iodide is described.

3. Solubility measurements are given for the temperature range 15 to 50°.

4. The constitution of these double compounds is discussed and their relation of photographic sensitizing.

ROCHESTER, NEW YORK

[CONTRIBUTION FROM THE DIVISION OF PLANT NUTRITION, UNIVERSITY OF CALIFORNIA]

PHOTOSYNTHESIS WITH MALACHITE GREEN

BY DEAN BURK

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According to Baly, Heilbron and Barker[1] and Baly,[2] "an aqueous solution of malachite green saturated with carbon dioxide yields formaldehyde on exposure to light behind a thick plate glass screen. In the absence of carbon dioxide no formaldehyde is produced." No details of technique in support of this claim were offered. Baur and Büchi[3] repeated the experiment, but they were unable to conclude that the formaldehyde came from the carbon dioxide. Indeed there was no doubt, from their experiments, that the presence of carbon dioxide in the exposed solutions of malachite green, the concentrations of which varied eight-fold, from 15 to 125 parts per million, reduced the yield of formaldehyde. When the absence of all carbonate or bicarbonate ions was insured by the addition of varying amounts of barium hydroxide, the yields of formaldehyde were increased decidedly, even though the solutions may have been partially or entirely discolored before exposure was made, owing to the alkalinity. The fact that the colorless solutions, when

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[8] Renwick, Baldsiefen and Sease, *Phot. J.*, **66**, 163 (1926).

[9] Sheppard, Wightman and Trivelli, *Trans. Faraday Soc.*, **19**, 296 (1923).

[10] Clark, *Phot. J.*, **64**, 91 (1924).

[1] Baly, Heilbron and Barker, *J. Chem. Soc.*, **119**, 1032 (1921).

[2] Baly, *Rec. trav. chim.*, **41**, 528 (1922).

[3] Baur and Büchi, *Helv. Chim. Acta*, **6**, 959 (1923).

exposed, gave relatively large amounts of formaldehyde, combined with the fact that the yield was reduced when the insolation was made behind glass walls of increasing thickness, strongly supported the view that only the colorless ultraviolet rays were responsible for the photochemical effect, and still further weakened the original conception of Baly, Heilbron and Barker that carbon dioxide could be reduced by *visible* light when a photochemical catalyst like malachite green, which may combine with it, is present also. Baly has since reversed his position, and has stated[4] that formaldehyde may form even in the absence of carbon dioxide. The present paper will offer evidence, obtained by experimental methods different from those previously used, which extends the general findings of these investigators.

Experimental Part

The new experimental feature of the technique was the use of condensed sunlight. The lenses were large, spherical, colorless, common glass flasks 30 cm. in diameter filled with clear water and mounted on stationary iron tripods. Calculations indicated that the intensity of sunlight which had passed through them was increased to a maximum of approximately 5000-fold; for noon sunlight this intensity would be about five million times that of an ordinary 40-watt Mazda lamp. Exposure behind one of these lenses on a clear day was considered to be equal, as regards the amount or total energy value of the light, to exposure to ordinary sunlight for about a month of clear days. (This assumption was confirmed experimentally by study of other relatively uncomplicated reactions, such as the reduction of Fehling's or Benedict's solutions, the decomposition of uranyl formate, etc., where justifiable interpretation was allowable because the rates of reaction were rapid enough and the equilibrium points far enough on the sides of the resultants.) The beam of light was generally 6 mm. in diameter at the point where it entered the exposed solution. The temperature of the solution was kept below 30° by immersion of the containing vessel a little below the surface of a simple water-bath. The solutions, whose concentrations in these experiments were always 50 parts per million (0.005%) of malachite green chloride, were exposed in glass bulbs blown on the end of common soft glass tubes about 30 cm. in length and 12 mm. in diameter. The bulbs were quite spherical, had a capacity of from 15 to 50 cc., were just as thin as safety would allow (from 0.05 to 0.1 mm.), and were very transparent. The tubes were cleaned with chromic acid at 100°, hot alcoholic potassium hydroxide, hot concd. nitric acid, and many rinsings of distilled water. (In order to allow for the movement of the sun, the positions of the bulbs were changed every 20 minutes. No heliostat was employed.) The tubes were exposed to lenses for four to six hours a day, but they also

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[4] Baly, *Ind. Eng. Chem.*, **16**, 1016 (1924).

received the ordinary sunlight during the remaining hours. A control tube containing a solution of similar composition, but protected from light by being heavily wrapped in tin foil, was placed beside each exposed tube, in the same thermostat. Since the two corresponding tubes were treated as exactly alike as possible (except that their volumes frequently differed), except for exposure, any difference found between their contents upon examination could be considered as having been caused by either primary or secondary effects of light. The unexposed tubes were numbered "a." The sealed tubes were first evacuated with a water pump. The unsealed tubes were protected by hoods of tin foil bent over in such a manner as to allow entrance of air but to exclude foreign matter. The water used to make up the solutions was twice distilled and had a conductivity not greater than 5×10^{-6} mhos.

The ammonium carbonate used was Baker's $(NH_4)_2CO_3NH_4CO_2NH_2$, mol. wt. 174.15; 0.18 cc. of the 35.0 N sulfuric acid used in Expts. 9 and 10 was required to neutralize 0.500 g. of it to full methyl orange. The acid was contained in a side arm sealed into the neck of the tube, and was not mixed with the rest of the contents until after vacuum sealing. *Ammonium* carbonate was used since, if formaldehyde and oxygen gas were the photochemical end-products of the reaction to be studied, the ammonia could possibly assist in removing both of them, by forming hexamethylenetetramine (and other bases) as well as nitrites and nitrates.

Expts. 1–6 and 11–12 were exposed to lenses for 19 hours during December 27 to 30. Expts. 7–10 were exposed to lenses for 25 hours during December 15 to 23.

Results and Discussion

Table I contains the results of the experiments selected for mention.

The magnitudes of the concentrations of formaldehyde found agree exactly with those observed by Baur and Büchi.[3] In acid solutions there was never more than 1 p.p.m. (part per million), generally much less; in the most alkaline solutions, 4 to 6 p.p.m. The Schryver test as employed by the writer was sensitive to 0.1 p.p.m., the Gallic acid test to exactly 1 p.p.m. This explains why in solutions where 1 p.p.m. or less was found by Schryver's, the Gallic test was negative. The standard solutions for comparison were made up in the presence as well as the absence of malachite green. At 1 p.p.m. of formaldehyde neither test is affected (within 10%) by the presence of 50 p.p.m. of malachite green, since the strong acidity of both sets of reagents instantly destroys the color of the dye. Baur and Büchi's statement that the presence of air makes little difference in the amount of formaldehyde formed is confirmed. Under the experimental conditions employed it would require a statistical study of many repeated experiments to show a real difference. The fact that the Gallic test, which is a good hydrolyzing agent on account

TABLE I

0.005% MALACHITE GREEN

No.	Treatment	Color of solution	Vol.,[a] cc.	*P*H	A[b]	B[c]	Schryver, p.p.m.	Gallic, p.p.m.	Nessler
1	Unsealed	Intense blue-green	52	6.5	0.00	6	0.6–1	None	Slight white ppt.
1a	Same, unexposed	Intense blue-green	41	6.5	.00	6	None	None	None
2	Unsealed, + 1 drop of concd. NaOH	Colorless, cloudy (yellow tinge)	35	>10	.03	2	4 –6	4–6	Slight white ppt.
2a	Same, unexposed	Colorless, cloudy	30	>10	.03	2	None	None	None
3	Unsealed, + H_2SO_4 to *P*H 2.0	Intense blue-green	25	2.0	.00	7	0.1–0.4	None	Very slight white ppt.
3a	Same, unexposed	Intense blue-green	15	2.0	.00	7	None	None	None
4	Sealed	Intense blue-green	30	6.5	.00	6	0.6–1	None	Slight white ppt.
4a	Same, unexposed	Intense blue-green	18	6.5	.00	6	None	None	None
5	Sealed, + 1 drop concd. NaOH	Colorless, cloudy (yellow tinge)	35	>10	.03	2	4 –6	4–6	Slight white ppt.
5a	Same, unexposed	Colorless, cloudy	31	>10	.03	2	None	None	None
6	Sealed, + H_2SO_4 to *P*H 2.0	Intense blue-green	30	2.0	.00	7	Tr. ? (0.1–0.2?)	None	Very slight white ppt.
6a	Same, unexposed	Intense blue-green	20	2.0	.00	7	None	None	None
7	Unsealed, + 0.50 g. of $(NH_4)_2CO_3$	Colorless, cloudy	36	8.6	1.0		2 –4	2–4	Heavy yellow-red ppt.
7a	Same, unexposed	Very light blue	48	8.3	1.0	2	None	None	Heavy yellow-red ppt.
8	Sealed, + 0.50 g. of $(NH_4)_2CO_3$	Colorless, cloudy	32	8.6	1.1		1 –2	1–2	Heavy yellow-red ppt.
8a	Same, unexposed	Very light blue	17	8.3	1.1	2	None	None	Heavy yellow-red ppt.
9	Same as 8, + 0.12 cc. of H_2SO_4	Intense blue-green	29	7.2	0.04		Tr. ? (0.1–0.2?)	None	
10	Same as 8, + 0.22 cc. of H_2SO_4	Blue	34	2.0	.04		Tr. ? (0.1–0.2?)	None	
11	Unsealed, + HCHO to 100 p.p.m.	Intense blue-green	35	6.5			100	100	Black-gray ppt.
11a	Same, unexposed	Intense blue-green	26	6.5			100	100	Dark brown ppt.
12	Sealed, + HCHO to 100 p.p.m.	Intense blue-green	24	6.5			100	100	Black-gray ppt.
12a	Same, unexposed	Intense blue-green	14	6.5			100	100	Dark brown ppt.

[a] Of solution.

[b] A = cc. of 0.1 *N* acid or base required to neutralize 1 cc.

[c] B = drops of 0.005 *N* permanganate required by 1 cc.

of the practically pure sulfuric acid which it contains, never indicates a greater concentration than does the Schryver test is good inferential evidence that little or none of the formaldehyde is being removed by the formation of condensation compounds with malachite green or any of its photochemical decomposition products, such as amines. This might be expected, perhaps, since at this dilution the free energies of such reactions would be unfavorable to condensation. These experiments make it plain why Baur and Büchi found that carbon dioxide decreased the concentration of formaldehyde observed and that barium hydroxide increased it; the amount is controlled by either the primary or secondary effects of the hydroxyl-ion concentration. The production of these small amounts of formaldehyde from malachite green was found by the writer to be practically independent, within ranges of 100-fold or more, of the intensity of the sunlight and the length of exposure (and the concentration of malachite green). Therefore, if solutions of from about 25 to 250 p.p.m. of malachite green were exposed to sunlight in the presence of carbonic acid (etc.) at a *P*H less than 10, the finding of perhaps five or more p.p.m. of formaldehyde would be, contrary to current opinion and the opinion of the investigators cited,[3] quite significant in relation to carbon dioxide reduction. In acid solutions, as little as 1 p.p.m. would be significant. This view is supported by the fact that while the maximum concentration of fomaldehyde which could form from a solution of 50 p.p.m. of malachite green, on the basis of all its carbon molecules, is 44 p.p.m. (88.2%), nevertheless, if the benzene ring carbon molecules are not considered, but only the four methyl radicals, the maximum concentration would be only seven p.p.m. (15.1%). While it is probable that the significant amounts suggested above have not been found by any workers, it must be remembered that the experimental conditions have been quite simple, and others might be devised where the desired result would be obtained. It is conceivable that conditions could be obtained where the amount of formaldehyde formed from the dye would be entirely unqualifying, that is to say, a concentration less than 0.1 p.p.m.

The potassium permanganate titration values indicate no significant change as regards the formation of reducing substances such as hydroxylamine and formic acid, since each exposed solution had the same value as its corresponding unexposed one.

The Nessler tests show that bases, presumably amines, are formed upon exposure. The amount of photochemical nitrogen decomposition as amines was greater by several times than the amount of carbon decomposition as formaldehyde. The amounts of amines found are smaller in acid solutions. The reaction is shown to be entirely photochemical.

The values for *P*H are accurate to 0.4, since the color of the dye interfered somewhat.

Expts. 7 to 10 show that the presence of ammonium, carbonate or bicarbonate ions, or of carbonic acid, have in no way affected the amount of formaldehyde formed, the *P*H being taken into consideration.

The following results could not be placed conveniently in the table.

Griess, Trommsdorff and diphenylamine tests were negative in all cases except Expts. 2 and 7, where the presence of 1 p.p.m. of nitrite was indicated, showing that for the oxidation of the ammonia or other decomposition products of malachite green, conditions of exposure to sunlight, aeration and alkalinity are necessary. The Griess and Trommsdorff tests were sensitive to 0.1 p.p.m., the diphenylamine to about 1 p.p.m. At 1 p.p.m. of nitrite, smaller amounts of nitrate also present could not be distinguished. The usual method of reducing the nitrate with zinc and testing for increase of nitrite by the Griess test, which is specific, would not suffice. The amount of nitrite formed is not dependent on the ammonium-ion concentration, since Expt. 7 contained much more of the latter than did Expt. 2. The role of air is not known, but simple absorption of atmospheric oxygen-nitrogen compounds is precluded by experiments not reported in which many unexposed, unsealed tubes were found never to contain nitrites. While ammonia may be oxidized to nitrates and nitrites by short-wave ultraviolet light[5] (200mμ), the oxidation of ammonia or ammonia-like forms, amines, etc., in the presence of sunlight-absorbing compounds, is not without example, as will be indicated in a later publication. The writer has found that ferric chloride, zinc oxide and mercuric oxide can oxidize ammonia to nitrites or nitrates in the presence of sunlight.

No odor was detected in any tubes, except that of ammonia in Expts. 7, 7a, 8 and 8a.

Reduction of Fehling's solution and the Molisch carbohydrate test were negative in all cases except, of course, in Expts. 11, 11a, 12 and 12a, where they were all of equal magnitude. No red ring was observed in the Molisch test, but rather the typical white cloud, insoluble in concd. sulfuric acid, given by formaldehyde.

All of the solutions except 2 and 2a gave the same slight black precipitate with iodine in potassium iodide solution (12.5 g. of iodine in a solution of 16.5 g. of potassium iodide in 100 cc. of water). When formaldehyde was added before the reagent (Thatcher test), all of the solutions gave the same kind and amount of precipitate except 2, 2a, 5, 5a, which gave smaller precipitates, and 11, 11a, 12, 12a, which gave also $C_6H_{12}N_4I_4$, hexamethylenetetraminetetra-iodide.

The writer wishes to express his appreciation of assistance and advice offered by Professor Dennis R. Hoagland.

Summary

1. While previous observations have indicated that malachite green decomposes in sunlight to yield formaldehyde, the present experiments show that amines are produced also, and in greater concentration than formaldehyde. When the conditions are aerobic and alkaline, nitrites are produced also.

2. The interpretation of photosynthetic experiments with malachite green solutions is prejudiced little if any by the formation of formaldehyde

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[5] Berthelot and Gaudechon, *Compt. rend.*, **152**, 522 (1911). Baly, Heilbron and Stern, *J. Chem. Soc.*, **123**, 185 (1923).

from the dye itself, since the order of magnitude of the concentration of formaldehyde is extremely small, without exception, and can be controlled at will by varying the experimental conditions, particularly of hydrogen-ion concentration.

BERKELEY, CALIFORNIA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF IOWA STATE COLLEGE]

THE REACTION BETWEEN CINNAMYL CHLORIDE, MAGNESIUM AND CARBON DIOXIDE

BY HENRY GILMAN AND STANTON A. HARRIS

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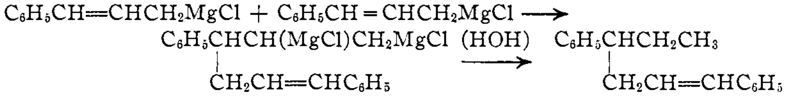
Introduction

In several quantitative studies, it has been proved that a few typical organomagnesium halides do not add to a wide variety of ethylenic and acetylenic hydrocarbons. Gilman and Crawford[1] used ethylmagnesium iodide with 11 ethylenic hydrocarbons; Gilman and Shumaker[2] used ethylmagnesium bromide and iodide with four acetylenic compounds; and Gilman and Peterson[3] used ethylmagnesium bromide, phenylmagnesium bromide, butoxymagnesium iodide, *p*-tolylmercaptomagnesium iodide, methylaniline-magnesium bromide and ethylzinc iodide with 18 variously substituted ethylenic compounds.

A recent book[4] and review[5] of the chemistry of organomagnesium halides direct attention to the work of Rupe and Bürgin[6] who have presumably proved that cinnamylmagnesium chloride (and bromide) adds to the ethylenic linkage of the cinnamyl group. They postulate the following reactions.



$$C_6H_5CH{=}CHCH_2MgCl + C_6H_5CH{=}CHCH_2MgCl \longrightarrow \underset{\displaystyle CH_2CH{=}CHC_6H_5}{C_6H_5CHCH(MgCl)CH_2MgCl} \xrightarrow{(HOH)} \underset{\displaystyle CH_2CH{=}CHC_6H_5}{C_6H_5CHCH_2CH_3} \qquad (1)$$

In support of the hydrocarbon (1,4-diphenyl-hexene-1) obtained by the addition of one molecule of cinnamylmagnesium chloride to the ethylenic linkage of another like molecule, they obtained phenylsuccinic and benzoic acids among the products of oxidation of their hydrocarbon. They were unsuccessful in their attempts to effect a reaction between the cinnamylmagnesium chloride (or bromide) and aldehydes or ketones. The hydrocarbon which they obtained in limited amounts after eight

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[1] Gilman and Crawford, THIS JOURNAL, **45**, 554 (1923).

[2] Gilman and Shumaker, *ibid.*, **47**, 514 (1925).

[3] Gilman and Peterson, *ibid.*, **48**, 423 (1926).

[4] Courtot, "Le Magnesium en Chimie organique," pp. 54, 318. Published by the author at Nancy, **1926.**

[5] Grignard, *Bull. soc. chim.*, **39**, 1285 (1926).

[6] Rupe and Bürgin, *Ber.*, **43**, 172 (1910).