poor radical derived from maleic anhydride with the slightly electron-rich double bond of the alkene is more favorable than the reaction with the electron-poor double bond of maleic anhydride. Thus, the enhanced favorability of propagation steps involving unlike radical and monomer relative to steps involving like radical and monomer follows logically. But using this approach, the conclusion does not follow that crossed allylic termination should also be enhanced. In fact the energy of activation for abstraction of an allylic or benzylic hydrogen by a radical derived from maleic anhydride would be predicted to be greater than that for abstraction by the radical derived from the phenylalkene. To the extent that polar interactions of reactants influence the activation energy, reaction of the electron-poor radical derived from maleic anhydride with allylic or benzylic hydrogens will be rendered less favorable by the inductive withdrawal on the part of the vinyl or phenyl group, leading to a lowering of the electron density in these bonds. To the extent that the transition state resembles products, the activation energy for the reaction involving the radical adjacent to a carbonyl group will be larger than that involving the secondary alkyl radical, because the former is a more stable radical and its destruction results in a correspondingly larger loss of resonance energy.

Thus, in a copolymerizing system of maleic anhydride and an alkene, propagation steps involving unlike radical and monomer are greatly enhanced, while allylic termination involving unlike radical and monomer is diminished in importance. These are the conditions necessary for the production of a high molecular weight polymer.

We feel that the many polar effects which have been reported in free radical forming reactions[1,21,22,30–35] can all be interpreted more simply in terms of polar interactions of reactants for low activation energy processes in which the transition state resembles reactants, or radical stability, the polar character of the radical being recognized,[29] for higher activation energy processes in which the transition state partakes of more of the character of the product radical; and that the postulate of transition state stabilization by electron transfer is unnecessary and in some cases leads to invalid predictions.

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Chlorination with Cupric Chloride

R. P. ARGANBRIGHT AND W. F. YATES

The reaction of pumice-supported cupric chloride with olefins was studied under temperature conditions which allowed the formation of dichlorides. The relative rates of reaction of various olefins and the stereochemistry of the products indicate that cupric chloride gives nonconcerted, stereospecific *trans* addition of chlorine to simple olefins. Homoconjugative addition was obtained with cupric chloride and norbornadiene.

The reaction of cupric chloride with hydrocarbons has been extensively studied at high temperatures (above 400°). Under such conditions the chlorine evolution from a copper chloride melt (containing potassium chloride) was found to be rate determining and the products obtained were those expected from a free radical chlorination,[1] for example, the reaction of methane to form methyl chloride.

We have been interested in the chemistry of the reaction of supported cupric chloride and olefins in a lower temperature range (220–330°) in which addition rather than substitution reactions occur.[2] For our study of the reaction, cupric chloride was supported on 40- to 100-mesh pumice and fluidized with nitrogen during its reaction with the olefin. The use of a fluid bed for the reaction allowed good temperature control, while the use of pumice allowed us to study the copper chloride reaction without the complicating effects of the more adsorbing and reactive supports such as the aluminas.

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(2) G. W. Hearne, U. S. Patent **2,399,488** (1946); A. J. Johnson and A. J. Cherniavsky, U. S. Patents **2,644,846** (1953) and **2,746,844** (1956).

The stoichiometry of the reaction follows the equation:

$$>C{=}C< + 2CuCl_2 \longrightarrow \underset{\underset{\displaystyle |}{|}}{Cl{-}C}{-}\underset{\underset{\displaystyle |}{|}}{C}{-}Cl + Cu_2Cl_2$$
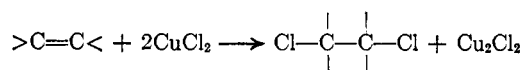
The temperatures which were found to be required for a smooth reaction of a number of olefins with pumice supported cupric chloride are shown in Table I. These reaction temperatures are in the

TABLE I

REACTION OF OLEFINS WITH CUPRIC CHLORIDE ON PUMICE

Olefin	Minimum Reaction Temp.[a]	Product, Mole %[b]
Butadiene-1,3	220	42% 3,4-dichlorobutene-1
		15% cis-1,4-dichlorobutene-2
		41 trans-1,4-dichlorobutene-2
		2% 1-chlorobutadiene
Acetylene[c]		92% trans-1,2-dichloroethylene
		2% cis-1,2-dichloroethylene
		6% 1,1,2-trichloroethylene
Butene-1	280–290	35% meso-2,3-dichlorobutane
		30% dl-2,3-dichlorobutane
		35% 1,2-dichlorobutane
cis-Butene-2	290	99% dl-2,3-dichlorobutane
		1% monochlorobutenes
trans-Butene-2	290	76% meso-2,3-dichlorobutane
		19% dl-2,3-dichlorobutane
		5% monochlorobutenes
Propylene	310–315	>90% 1,2-dichloropropane
Ethylene	325	>90% 1,2-dichloroethane

[a] Minimum reaction temp. is the lowest temp. required for a smooth reaction. See Experimental under *General methods of conducting the reaction of cupric chloride and olefins.* [b] Mole % values were estimated by GLPC analysis. [c] Min. reaction temp. was not determined. Reaction was carried out at 240–250°.

same order as the relative rates of reaction of the olefins—that is, butadiene >> butene-1 ≅ butene-2 > propylene > ethylene. As shown in Table II,

TABLE II

REACTIONS OF MIXED OLEFINS WITH CUPRIC CHLORIDE ON PUMICE

Mixed Feeds	Temp. of Reactor	Products
Butene-2 + butadiene (80:20 by vol.)	300–330	Products of butadiene chlorination only
Isobutene + ethylene (50:50 by vol.)	320–340	Products of isobutene chlorination only
cis-Butene-2 + trans-butene-2 (44:56 mole ratio)	300	47% dl-2,3-dichlorobutane—53% meso-2,3-dichlorobutane

mixed feeds of butadiene and *n*-butenes gave only the products of butadiene chlorination, provided that the butadiene flow rate exceeded its rate of reaction, and mixed feeds of isobutylene and ethylene gave only the products of isobutylene chlorination. A competitive reaction of *cis*- and *trans*-butene-2, however, gave the products from

the reaction of both olefins with the *cis* isomer reaction 1.1 times faster than the *trans* isomer.

Stereospecific *trans* addition was obtained by the reaction of cupric chloride with acetylene and with *cis*-butene-2. With *trans*-butene-2, *trans* addition predominated giving about 75% *meso*-2,3-dichlorobutane with 19% of the *dl* isomers.

To investigate further the ability of cupric chloride to give *trans* addition of chlorine to olefins, it was allowed to react with the bicyclic olefin, norbornadiene (I). It appeared possible, as this is a reaction on a surface, that homoconjugative addition, which is a common mode of reaction for the norbornadiene system[3,4] might not occur due to an inability of the bicyclic molecules to approach the salt surface in the required manner. In such a case, two possible products could result: (1) A 5,6-*trans*-dichloronorbornene formed *via* a chloronium ion reaction or (2) a *cis-exo*-5,6-dichloronorbornene which might be formed due to protection of the *endo* side of the reaction double bond by participation of the electrons from the remaining double bond. However, it was determined by infrared analysis that norbornadiene (I) and cupric chloride gave essentially the same product distribution as that obtained by the dark addition of chlorine in carbon tetrachloride at 5–15°. The principal product (about 90%) of this reaction appears to be 3,5-dichloronortricyclene (II), as its infrared spectrum has the prominent absorption band at 12.2–12.4 μ which is a characteristic of the nortricyclene structure.[5] This product was undoubtedly formed
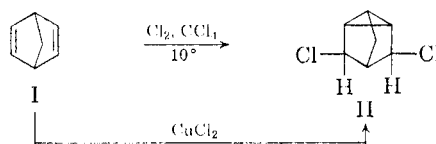
by a 1,5-homoconjugate addition in the dark chlorination reaction, as there is no reason to believe it different from the thoroughly studied reaction of bromine and norbornadiene.[3,4] The same result obtained by the gas phase reaction implies that the cupric chloride reaction is nonconcerted (a conclusion supported by the relative rates of reaction) and that there is no extra steric hindrance (compared, for example, with butene-2) against the approach of the norbornadiene to the cupric chloride surface. An alternative explanation would be that a 5,6-dichloronorbornene is formed initially which then thermally rearranges. This explanation is unlikely, as it would require the formation of radicals which would probably react in some

(3) L. Schmerling, J. P. Luvisi, and R. W. Welch, *J. Am. Chem. Soc.,* **78**, 2819 (1956).

(4) S. Winstein and M. Shatavsky, *Chem. & Ind.,* **56** (1956); *J. Am. Chem. Soc.,* **78**, 592 (1956).

(5) J. D. Roberts, E. R. Trumbull, Jr., W. Bennett, and R. Armstrong, *J. Am. Chem. Soc.,* **72**, 3116 (1950).

manner other than simple rearrangement. We cannot visualize a radical pair intermediate which would be required for facile rearrangement.

The relative order of reaction rates and the predominant *trans* addition are what one would expect from an electrophilic reaction[6] via a chloronium ion.[7] The extremely fast rate of reaction of butadiene relative to the olefins can be accounted for by considering the resonance stabilization of a conjugated intermediate.

The chlorinating agent cannot be adsorbed chlorine, however, since some substitution reactions would certainly have occurred at the temperatures used.[8] A reasonable explanation is that the chlorinating agent is cupric chloride itself and that it is much more selective than molecular chlorine due to a higher activation energy required for its reaction with an olefin.

A heterogeneous reaction of this type can generally be considered in three major stages,[9] adsorption, reaction, and desorption. In general, one of these steps will control the over-all observed rate of reaction. In this particular case the rate of desorption cannot be controlling the over-all rate, as the slowest reactions are those which give products which are saturated halides and which, therefore, should be desorbed the fastest, relative to the allylic halides. Also, the presence of product in the feed does not appear to inhibit the reaction.

A qualitative examination of the over-all reaction indicated that product was formed at a constant rate. This suggests that adsorption is the rate controlling step since, if the reaction step were the slow step, the rate of product formation would depend on the amount of cupric chloride available and therefore would decrease as the reaction progressed.

It seems very unlikely that the olefins complex with the copper ion, either cupric or cuprous, in the adsorption step since one should expect a relationship with coordination in solution[10a-c] and, therefore, the least substituted olefins should adsorb the fastest, and butadiene should be not much faster than the alkenes.[10b]

However, the olefins could be adsorbed in such a manner that the olefin coordinates with a chlorine atom of the copper salts on the surface. Then reaction could occur to form a chloronium ion, followed by a fast reaction of this intermediate

with chloride ion and then desorption of the dichloride product. The charged intermediates are probably stabilized by interaction with the surface of the copper chloride.

EXPERIMENTAL

Description of reactor. The reactor was a 4.8 × 100 cm. Pyrex tube wrapped with nichrome wire for heating purposes and insulated with asbestos. A glass thermowell (6 mm.) was centrally positioned inside the reactor so that a movable thermocouple could be used. At the bottom of the reactor was a gas inlet tube preceded by a mixer and preheater. A tube from the top of the reactor allowed the off gas to flow through a glass wool filter and then through a water cooled condenser to a Dry Ice–cooled condensing system wherein the products were collected. Noncondensable gases were allowed to flow through a sodium hydroxide scrubber into a gas meter and 'were then vented. The flow rates of the reactants and nitrogen diluent were measured at room temperature with rotameters.

If it were necessary to feed a high boiling liquid, as in the case of norbornadiene, it was fed directly from a burette into the preheater.

Preparation of cupric chloride on pumice. Sixty grams (0.35 mole) of cupric chloride dihydrate was dissolved in 200 ml. of methanol. This solution was then added to about 300 ml. of pumice (40–100 mesh) while the pumice was under vacuum in an evacuated flask. The excess solution was filtered off and the treated pumice was dried in a vacuum oven at 60–70° for about 6 hr. The material was then placed in the reactor and was further dried to 300° by a flow of nitrogen.

General method of conducting the reaction of cupric chloride and olefins. After drying the pumice supported cupric chloride in the reactor, the reactor was cooled to about 150° and the bed was fluidized with a flow of nitrogen (1.5 l./min.). Then the olefin to be reacted was added at 600 ml./min. and the reactor was heated until it was apparent that a product was being formed by the presence of liquid condensing in a water-cooled condenser preceding the trap system. When the product was formed at a rate sufficient to give about 2 drops of liquid every 3 sec. off the condenser tip, the reactor temperature was recorded as the minimum temperature required for a smooth reaction of the olefin. This temperature was, in every case, within 10° of the initial appearance of product.

The condensable materials were then collected from the traps and the olefin reactant was removed by distillation. The remaining material was separated by gas-liquid partition chromatography (using a polypropylene glycol on Chromasorb column) and the fractions were identified by their infrared spectra.

The cupric chloride could then be regenerated by the addition of hydrochloric acid and air at about 300° but, generally, fresh cupric chloride was prepared for each olefin reaction.

Stoichiometry of the reaction. A bed of cupric chloride was prepared which contained 0.29 mole of cupric chloride on pumice. This was allowed to react to completion with butadiene at 240–250°. A total of 0.12 mole of mixed dichlorobutenes was recovered from the Dry Ice traps. The theoretical yield from the reaction $C_4H_6 + 2CuCl_2 \rightarrow C_4H_6Cl_2 + Cu_2Cl_2$ would be 0.14 mole of $C_4H_6Cl_2$.

The cupric chloride was regenerated with hydrochloric acid (600 ml./min.) and air (1000 ml./min.) at 280–300° for 10 min. Butadiene was again added under conditions described above and formed 0.11 mole of dichlorobutenes.

Stereospecific trans addition to butene-2. Pure *meso-* and *dl-*2,3-dichlorobutanes were prepared by the method of Lucas and Gould[11] from pure *trans-* and *cis-*butene-2 isomers. The

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(7) I. Roberts and G. E. Kimball, *J. Am. Chem. Soc.*, **59**, 947 (1937).

(8) F. F. Rust and W. E. Vaughn, *J. Org. Chem.*, 472 (1940).

(9) K. J. Laidler, *Catalysis*, Vol. 1, H. Emmett, ed., Reinhold, New York, 1954, p. 128.

(10) (a) R. N. Keller, *Chem. Revs.*, **28**, 229 (1941). (b) S. Winstein and H. J. Lucas, *J. Am. Chem. Soc.*, **60**, 836 (1938). (c) W. S. Dorsey and H. J. Lucas, *ibid.*, **78**, 1665 (1956).

(11) H. J. Lucas and C. W. Gould, Jr., *J. Am. Chem. Soc.*, **63**, 2541 (1941).

meso- and *dl*-dichlorobutane products were separable by GLPC.

The infrared spectra of the pure isomers were compared with the spectra obtained from the products of the reactions of pure *cis-* and *trans*-2-butenes with cupric chloride on pumice at 290°. It was determined that *dl*-2,3-dichlorobutane was formed from the reaction of *cis*-butene-2 while the *meso*-isomer was predominantly formed by the reaction of *trans*-butene-2 with cupric chloride.

Chlorination of norbornadiene. Forty-six grams (0.5 mole) of norbornadiene was dissolved in 100 ml. of carbon tetrachloride in a black, three neck flask equipped with a stirrer, condenser, and gas inlet tube. At 15°, chlorine was added at a rate of about 150 ml./min. over a 60-min. period (0.4 mole of chlorine). The material was then distilled through a small

Vigreux column to give two product fractions: (1) 3.5 g., b.p. 67–78°, at 14 mm.; and (2) 28.5 g., b.p. 79–80°, at 8 mm. Cut (1) was not identified. Cut (2) was identified as 3,5-dichloronortricyclene by analysis of its infrared spectra.[5] This product was the same as the major product (>90%) obtained by the reaction of norbornadiene and cupric chloride on pumice at 285°.

Oxidation of Protocatechuic Acid with Peroxyacetic Acid

L. R. MORGAN, JR.[1]

Treatment of protocatechuic acid with peroxyacetic acid has heretofore resulted in fission of the carbocyclic ring and formation of β-carboxy-*cis*, *trans*-muconic acid (III) and β-carboxy-γ-carboxymethyl-$\Delta^{\alpha,\beta}$-butenolide (IV). Evidence has been reported which supports the stereochemical orientation.

We wish to describe at this time the chemical conversion of protocatechuic acid (I) to β-carboxy-*cis*,*trans*-muconic acid (III) and *dl*-β-carboxy-γ-carboxymethyl-$\Delta^{\alpha,\beta}$-butenolide (IV).

The oxidation of protocatechuic acid (I) to 4-carboxybenzoquinone-1,2 (II) is preferably carried out with silver oxide. The absorption spectrum of the quinone exhibits a maximum extinction at 420 mμ (log ϵ 3.12).[2] Treatment of the freshly prepared quinone with peroxyacetic acid[3] results in a geometrical isomer of β-carboxymuconic acid (III) and β-carboxy-γ-carboxymethyl-$\Delta^{\alpha,\beta}$-buteno-lide (IV).[4,5] We find in each case that the melting points of III and IV vary with the rate of heating, which probably accounts for apparent discrepancies in the literature.[4a,6]

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(2) The quinone chromophor is similar to that of *o*-benzoquinone, λ_{max} 390 mμ (log ϵ 3.26) [*cf.* F. Ramirez and P. V. Ostwald, *J. Org. Chem.*, 20, 1676 (1955)] and *N*-benzoyl-6-methoxydopamine, λ_{max} 220 and 375 mμ [*cf.* S. Senoh and B. Witkop, *J. Am. Chem. Soc.*, 81, 6222 (1959)].

(3) J. H. Boyer and L. R. Morgan, Jr., *J. Am. Chem. Soc.*, 83, 919 (1961).

(4) (a) D. L. MacDonald, R. Y. Stanier, and J. L. Ingraham, *J. Biol. Chem.*, 219, 809 (1954). (b) E. L. Tatum and S. R. Gross, *ibid.*, 219, 707 (1956).

(5) On the basis of physical and chemical properties, III appears to be identical to the biologically inactive (*cis*, *trans*-) β-carboxymuconic acid isolated by MacDonald, Stanier, and Ingrahm and IV, undoubtedly a racemate of their $\Delta^{\alpha,\beta}$-butenolide.

(6) S. R. Gross, R. D. Gafford, and E. L. Tatum, *J. Biol. Chem.*, 219, 781 1956).
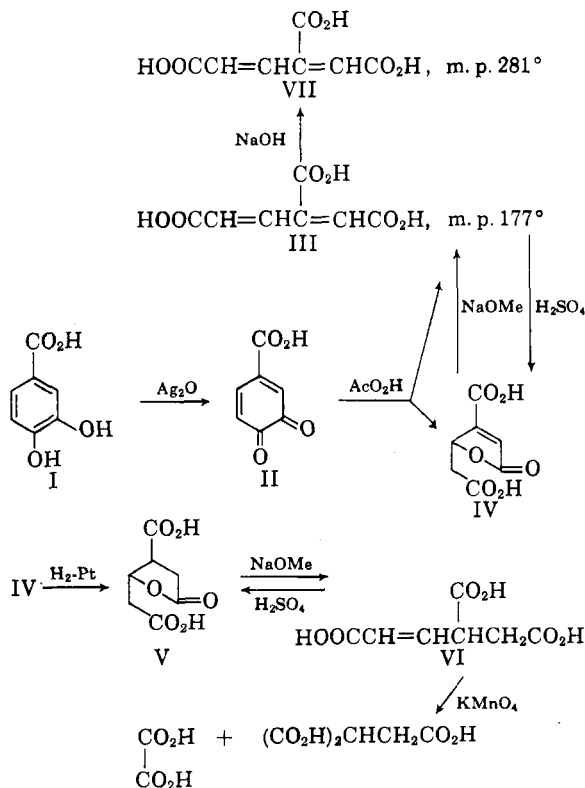
Hydrogenation of the β-carboxymuconic acid (III) over platinum results in the uptake of two molecules of hydrogen and the formation of β-carboxyadipic acid. Lactonization of III with dilute sulfuric acid affords β-carboxy-γ-carboxymethyl-$\Delta^{\alpha,\beta}$-butenolide (IV) which can be re-