

recently queried this mechanism on similar, but qualitative, grounds.

Summary

(1) A change of rate-determining step with pH occurs in the acylation of chymotrypsin by some specific hydrazide substrates and also by some anilide substrates. (2) This implies the existence of an additional intermediate between the Michaelis complex and the acylchymotrypsin. (3) This intermediate does not appear

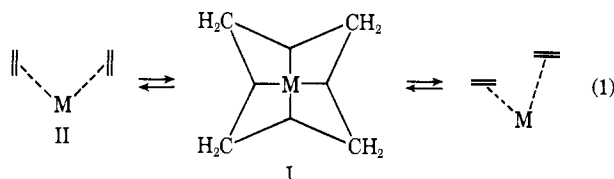
to be an oxazolinone. (4) A possible interpretation consistent with experimental observations, model studies, and structure–reactivity considerations is that a tetrahedral intermediate is formed in a low steady-state concentration; at high pH its breakdown is rate determining and at low pH its formation is the rate-determining step. (5) The binding of ligands to α -chymotrypsin is controlled by three ionizing groups on the enzyme of pK_a values ~ 5.3 , 7.0, and 8.8. (6) The pre-transition-state protonation theory is inadequate in its description of these reactions.

Communications to the Editor

On the Mechanism of the Metal-Catalyzed Disproportionation of Olefins

Sir:

The disproportionation reaction of olefins, effected by various transition metal catalysts, is one of the unique types of transformations discovered in recent times and considerable interest lies in the mechanism of the process, particularly the role played by the metal atom. We have recently proposed that the reaction proceeds *via* reversible transformation of two coordinated olefinic bonds into a multi-three-centered species I in which four CH_2 units of sp^3 -hybridized carbon atoms are involved (eq 1).¹ For convenience the spe-



cies I is referred to as the tetramethylene complex and is to be equated with the terms “quasicyclobutane”² and “pseudocyclobutane”³ used during the early studies of this reaction. Two virtues of this mechanistic scheme are that it avoids invoking a cyclobutane ring structure as an intermediate (cyclobutanes are not products of the reaction, and olefins are not converted into cyclobutanes under the disproportionation reaction conditions).⁴ In addition, the scheme offers an explanation of the role played by the metal atom in removing the “forbiddenness,” according to the Woodward–Hoffmann rules of orbital symmetry, associated with the overall reaction.⁵

In each of the systems discovered so far,⁶ in no case

(1) G. S. Lewandos and R. Pettit, *Tetrahedron Lett.*, 789 (1971).

(2) C. P. C. Bradshaw, E. J. Howman, and L. Turner, *J. Catal.*, 7, 269 (1967).

(3) E. A. Zuech, *Chem. Commun.*, 1182 (1968).

(4) Molybdena on alumina converts cyclobutane into ethylene (3% yield) and ethylene into cyclobutane (0.1% yield) at long contact times, but these two processes are very much slower than disproportionation under the same conditions.¹

(5) R. B. Woodward and R. Hoffmann, “The Conservation of Orbital Symmetry,” Verlag Chemie–Academic Press, Germany, 1970, and references therein.

(6) G. C. Bailey, *Catal. Rev.*, 3, 37 (1969), and references therein; N. Calderon, *Accounts Chem. Res.*, in press, and references therein.

has the active catalyst species been identified; they all involve metal systems of unknown character deposited on metal oxide surfaces, or substances derived from metal complexes together with Lewis acid or base cocatalysts. We have discovered that $W(CO)_6$, $Mo(CO)_6$, and arene- $W(CO)_3$ complexes can act as homogeneous catalyst precursors for the disproportionation of olefins, and although they are not notably effective as catalysts, their simplicity has allowed for a more detailed mechanistic investigation. With these catalysts we now report data consistent with the proposed mechanism given by eq 1.

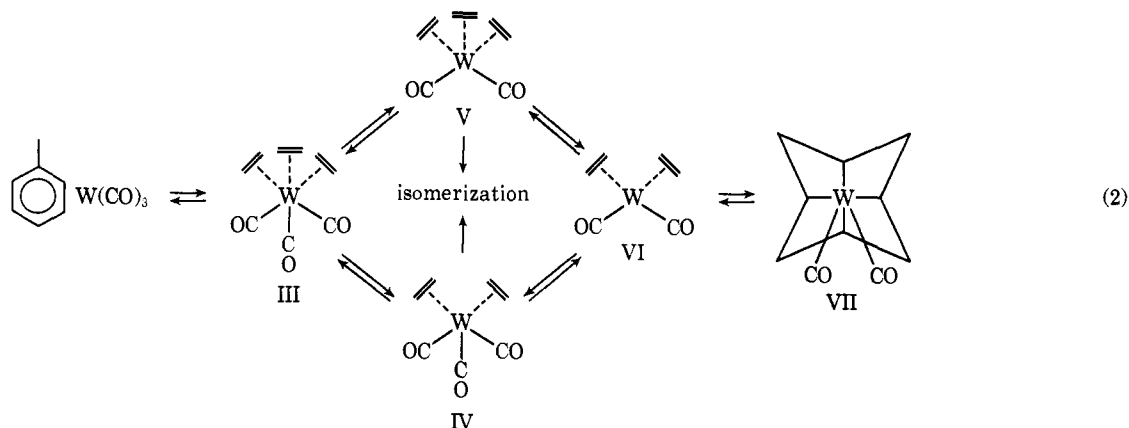
An interesting feature of the proposed mechanism is that in proceeding from the bisolefin metal system II to the tetramethylene complex I the number of donor electrons provided by the organic ligands increases from 4 to 8. It is widely recognized that the most thermodynamically stable complexes of metals in zero or low oxidation states are those in which the effective atomic number rule (EAN), or inert gas rule, is obeyed.⁷ Complexes in which the number of electrons about the metal falls short of the next inert gas are known, but species in which the number of donor electrons causes the next inert gas structure to be exceeded do not appear to exist. They are certainly high-energy species and are unlikely to be species involved in any catalytic reaction. It is significant that in none of the reactions catalyzed by transition metals in low-oxidation states are species proposed in which the number of electrons about the metal exceeds that of the next inert gas (the hydroformylation of olefins catalyzed by $HCo(CO)_4$ ⁸ and the cyclooligomerization of butadiene catalyzed by Ni complexes⁹ are good examples).

If the scheme depicted in eq 1 is correct and the transformation $II \rightarrow I$ involves an increase in donor electrons from 4 to 8 then only two other CO ligands can be present on the W atom in the tetramethylene complex I if the next inert gas configuration is not to be exceeded. That is, in addition to toluene, one molecule of CO must be removed from the tungsten atom in toluene- $W(CO)_3$ in order to generate the true catalytic species. A more detailed mechanistic scheme can

(7) N. B. Sidgwick, *Trans. Faraday Soc.*, 19, 469 (1923).

(8) R. F. Heck and D. S. Breslow, *Advan. Chem. Coord. Compounds*, 281 (1961).

(9) G. Wilke, *Angew. Chem., Int. Ed. Engl.*, 2, 105 (1963).



therefore be proposed (eq 2). Replacement of toluene by olefin generates the trisolefin- $W(CO)_3$ complex III which, upon loss of olefin or CO, would generate the bisolefin- $W(CO)_3$ IV or the trisolefin- $W(CO)_2$ V, respectively. Further loss of olefin from V would provide the bisolefin- $W(CO)_2$ species VI in which the two olefinic ligands can now undergo disproportionation *via* the tetramethylene- $W(CO)_2$ complex VII.

Results of the reaction of 4-nonene with toluene- $W(CO)_3$ under a variety of conditions are listed in Table I. These data are clearly consistent with the scheme

Table I. Distribution of Products from Reaction of 4-Nonene with Toluene-tungsten Tricarbonyl

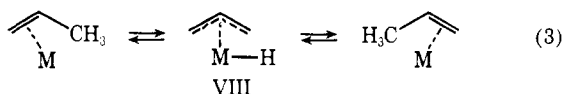
Conditions ^a	mmol of 4-nonene	% disproportionation ^b	% isomerization ^c
1. Open system	0.258	28	6
2. Closed system ^d	0.258	0	<1
3. Open system, excess olefin	7.00	2	5
4. Closed system, excess olefin	7.00	0	<1
5. Open system, excess toluene ^e	0.258	2	~0

^a All reactions were conducted for 24 hr at 98° in the presence of 0.070 mmol of toluene-tungsten tricarbonyl in 0.95 ml of heptane. The starting nonene was a mixture of *cis-trans* isomers. ^b The maximum theoretical per cent disproportionation is ~50%. After about 20% conversion, secondary disproportionation products began to appear. ^c Due to the possibility that our vpc column could not separate all the isomers of nonene, the yields of isomerization reported represent minimum yields of isomerization. ^d Results obtained after 17 hr at 98°. After an additional 48 hr at 120°, there was still observed no disproportionation although 33% isomerization was found. ^e Excess toluene (0.48 ml, 4.52 mmol) and less heptane (0.47 ml) were employed.

depicted in eq 2. The principal features of the data are summarized below.

When 4-nonene is treated with toluene- $W(CO)_3$ in heptane at 98° in an open system, disproportionation of nonene to octenes plus decenes occurs, together with a little isomerization, and both toluene and CO are found in the reaction products (line 1). When the same reaction is conducted in a closed system, thus preventing the escape of CO, no disproportionation of nonene occurs, but isomerization is observed (line 2). Toluene is again produced as a reaction product. The fact that isomerization still proceeds under these conditions is readily accounted for by the scheme shown in eq 2. The pathway available for isomerization of olefins by metal carbonyls involves reversible transformation of

a coordinated olefin to a π -allyl metal hydride VIII, eq 3.¹⁰ In proceeding from the olefin to the π -allyl



system VIII the number of donor electrons increases by only 2; hence the bisolefin- $W(CO)_2$ species IV can still effect isomerization in the closed system. When the reaction is conducted in an open system (line 3) in the presence of excess nonene the reaction proceeds but leads to a very much increased ratio of isomerization as compared to disproportionation; that is consistent with the formation of the complex V and inhibition of its conversion to VI. When the reaction is conducted in a closed system in the presence of a relatively large excess of nonene, then toluene is liberated but neither disproportionation nor significant isomerization occurs (line 4); this again is in full accord with the equilibria shown in eq 2. These latter conditions favor the formation of the trisolefin- $W(CO)_3$ complex III which of course is not a catalyst for either reaction. The addition of toluene (line 5) also inhibits both isomerization and disproportionation as would be expected from the mechanistic scheme.

Results analogous to those reported for nonene have been obtained for reactions of 2-pentene, styrene, and 1,7-octadiene.

These data are clearly in accord with the hypothesis that both toluene and carbon monoxide must be removed from the arene- $W(CO)_3$ before two coordinated olefinic molecules are able to undergo disproportionation as required by the scheme outlined in eq 2.

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(10) W. T. Hendrix, F. G. Cowherd, and J. L. von Rosenberg, *Chem. Commun.*, 97 (1968).

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Photochemically Induced Reversible Color Changes in Cholesteric Liquid Crystals

Sir:

The very sensitive dependence of the pitch of cholesteric liquid crystals on weak external physical perturba-