COMMUNICATION

ON THE MECHANISM OF 1- OCTENE ISOMERIZATION AND HYDROSILYLATION REACTION CATALYSED BY $Ru_3(CO)_{12}$

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ملخص

تم في هذه الورقة دراسة تفاعلات التشكل واضافة السايلان الى الالكيـــن الطرفـــي (١-أوكتين) باستخدام الحفاز 1. وقد بينت النتائج ان الألكين الطرفي يتشكل فقط بوجود السايلان وعلى درجة حرارة ٦٠°م فأقل ، ويعطي ض -٢- أوكتين، في حين أنه على درجة حرارة ٧٠°م فأكثر يحصل تفاعل اضافة السايلان الى الأوكتين الطرفي بالاضافة الى تفاعل التشكل . من هذه النتائج ومن الدراسة الحركية لهذين التفاعلين تم اقتراح ميكانيكية محتملة لكلا التفاعلين .

Isomerization and hydrosilylation reactions of terminal olefins have been reported under thermal and photochemical conditions using $Ru_3(CO)_{12}$, 1, and $HRu_3(CO)_{11}$, 2,[1-5].

In a very recent work, we reported[1] that 1 catalyses both Isomerization and hydrosilylation reactions of 1 - octene (eq. 1). It has been found that the isomerization reaction occurs via lower nuclearity catalytic species that result from fragmentation of the mother cluster 1. Evidence in favour of concurrent cluster catalysis

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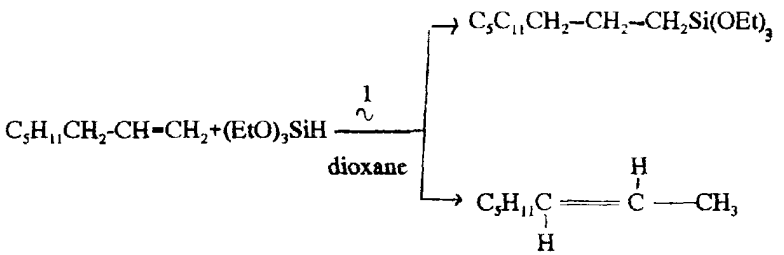
was also reported. On the other hand, the hydrosilylation reaction occurred via cluster catalysis at first and after some-time fragment catalysis occurred[1].



In this communication, we report our discussions regarding plausible mechanistic pathways for the hydrosilylation and isomerization reactions of 1 - octene using cluster 1.

EXPERIMENTAL

All chemicals used were purchased from Aldrich Chemical Co. in pure form. IR spectra were measured on a Pye Unicam SP200 spectrophotometer.

Catalytic experiments were conducted as follows : a stirred thermostated 100 ml round - bottomed flask reactor was charged with the cluster, the solvent dioxane (enough to make total volume 10.0 ml), the silane and the internal standard reference (benzene , 5.0 ml). The olefin was then syringed via a suba-seal stopper. A cooled condenser column was connected to the reactor to prevent evaporation.

Throughout the course of the reaction, small aliquot were taken after specified times. Each aliquot was immediately chilled in a stoppered sample tube, and then IR analyzed.

The hydrosilylation reaction was monitored by following the rate of disappearance of Si- H IR band at 2210cm^{-1} relative to the standard reference band at 1960 cm^{-1}. The isomerization reaction was monitored by two methods. In one method, the appearance of the product $C_5H_{11}(CH_2)_3Si(OEt)_3$, 2, was monitored. This was achieved by measuring the 1250cm^{-1} IR band relative to reference band at 1960cm^{-1}. In the other method, the isomerization reaction was monitored by following the rate of consumption of 1-octene (IR band at 1650cm^{-1}) less the rate of consumption of $(EtO)_3SiH$ (IR band at 2210cm^{-1}).

RESULTS AND DISCUSSION

The Isomerization Reactions:

At 60°C or lower, 1- octene underwent the isomerization reaction. Only ... trans- 2-octene was detected. No isomerization reaction occurred in the absence of the silane. Turnover number (T.N= moles of trans- 2-octene/ moles of 1) values of up to 700 were obtained within 11 min. The product was identified by its boiling range (120-122°C). Fingerprint IR spectral comparison of reaction product with literature[6] values and with authentic sample spectra were conclusive.

The reactions showed a first order dependence on the silane and on the olefin, when relatively low concentrations were used (2.0 and 1.0M or lower for the olefin and the silane respectively). These

results were obtained by the method of initial rates. Plots of ln(initial rate) vs. ln[reactant] were constructed.

At 70°C or higher, similar results have been obtained with higher T.N. values (higher than 700 within 11 min.).

However, at 70°C or higher, the olefin isomerization was not the only reaction that took place, vide infra. The reaction has been conducted at different temperatures ranging from 50 to 70°C. The activation energy has been calculated and found to be 25.0 Kcal mol^{-1}. Below 45°C, no detectable reaction was observed. In the temperature range 60-70°C, mixtures of isomerization and hydrosilylation reaction products were observed[1].

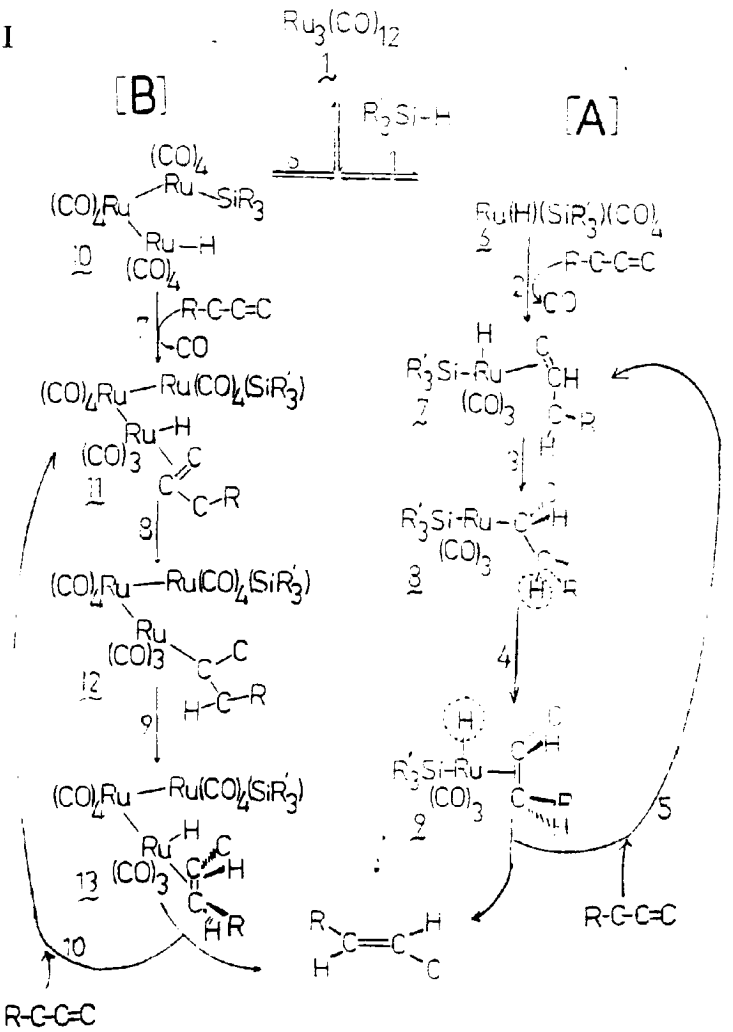
As reported earlier[1] the Laine's kinetic criterion[7] has been used to see if catalysis occurs by the intact cluster $\underset{\sim}{1}$ or by other fragment species that may result during the reaction. The results indicated a fragment catalysis with the possibility for concurrent cluster catalysis[1].

To account for the above results. a two - route mechanism, which presents both cluster and fragment catalytic pathways, has been proposed(scheme I).

Steps (1) and (6) show the role of the tertiary silane in activating the cluster. $\underset{\sim}{1}$ is known to be unreactive to molecules such as olefins[8]. This explains the lack of isomerization in the absence of the tertiary silane. It is well established that $\underset{\sim}{1}$ becomes more reactive when activating ligands are added such as $\underset{\sim}{CH_3CN}$[9], Ph_2PH[10-11] and others[12]. Oxidative- addition of the Si-H addendum at metal atom

clusters has been proposed for other catalytic systems[13]. It is assumed here that the equilibrium in step (1) should be shifted more toward the reactant side, videlicet $k_1 < k_{-1}$. This was evidenced by the lack of significant shift in the catalytic mixture visible spectra. This assumption is also consistent with theory. In step (1), the forward reaction

Scheme I



R- = C_5H_{11}-

involves an increase in the Ru formal oxidation state. Such process is not favored in metal atoms that are surrounded by π-acidic CO ligands.

Each catalytic cycle shown in Scheme I explains the kinetics. Assuming that step (1) is a quickly established equilibrium, and that step (2) in cycle A, (or step 7 in cycle B), is a slow step, and using steady state approximation,[14], for $\underset{\sim}{6}$ in cycle A (or for $\underset{\sim}{10}$ in cycle B) then:

$$rate = \frac{k_1 k_2}{k_{-1} + k_2[olefin]} \cdot [Ru_3(CO)_{12}]\ [(EtO)_3SiH][olefin]$$

At low olefin concentrations, and knowing that step (2) is slow, viz $k_{-1} >> k_2$, then:

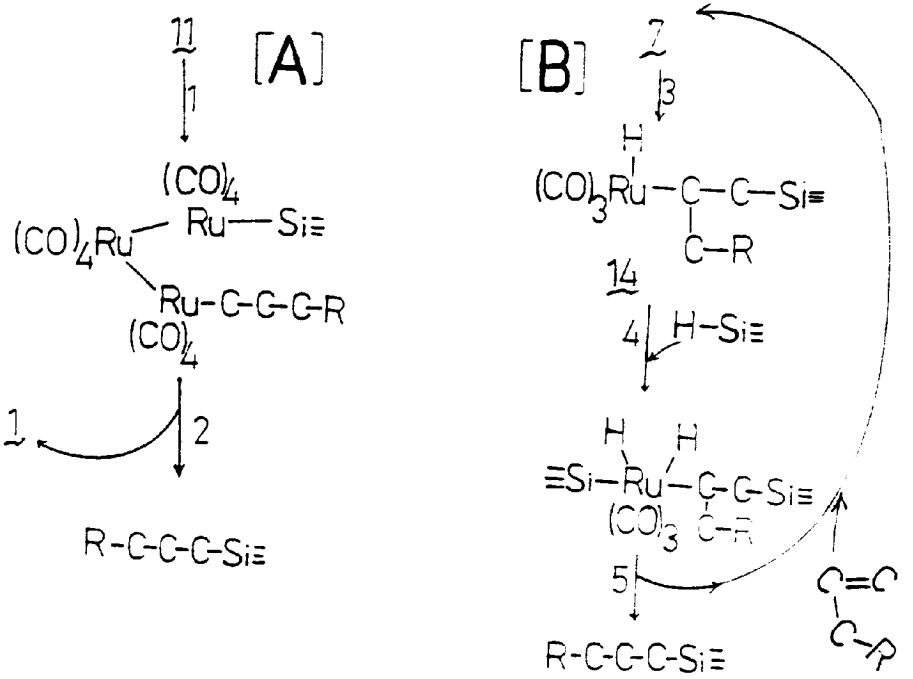
$$rate = \frac{K_1 K_2}{k_{-1}} \cdot [Ru_3(CO)_{12}]\ [(EtO)_3SiH][olefin]$$

which is consistent with the experimentally determined kinetics[1]. Step (3) is an insertion reaction that is well known for many other catalytic systems[15]. Step (4) is a deinsertion reaction that is well known[1]. Step (5) is a Lewis base dissociation reaction, followed by a lewis base association reaction to form 7.

The Hydrosilylation Reaction:

In a recent study of the 1- octene hydrosilylation reactions[11], it has been stated that cluster catalysis occurred at the beginning of the reaction. After 15 min, indication of concurrent fragment catalysis were apparent. Based on the discussion of Scheme I, vide supra, Scheme II has been proposed. Scheme II shows two reasonable pathways for the 1-octene hydrosilylation.

Scheme II



Path A involves catalysis by intact cluster. Step (1) is an insertion of the olefin molecule between Ru and H in complex $\tilde{11}$. This is an anti-Markovnikov's process. Step (2) is a binuclear reductive-elimination of the product molecule.

Path B involves catalysis by fragment species. Step (3) is an insertion reaction of the olefin molecule between Ru and Si atoms. Step (4) is an oxidative-addition of a new silane molecule to completethe sixteen valence shell electrons at Ru. Step (5) is a reductive-elimination, of the product molecules, followed by a Lewis base association. Similar reaction pathways are well known[16].

ACKNOWLEDGMENTS

This work has been conducted in full in the laboratories of An-Najah National University. The authors wish to thank S.Al-Dado, E.M. Sawalha, H. Diab, S. Abu-Baker, O. Doud, N. Taha, and A. Al-Sayed, all of this department.

REFERENCES

1. Hilal, H.S.; Jondi, W.; and Khalaf, Sh.; J.Organometal. Chem.,452 (1993), 167.
2. Kaspar, J., J. Mol. Catal., 48 (1988) 29.
3. Kaspar, J., J. Organometal Chem., 281 (1985) 299.
4. Castiglioni, M.; Mildne, L.; Osella, D.; Vaglio G.A. and Valle M.; Inorg. Chem., 15 (1976) 396.
5. Suss-Fink and Reiner J.; J. Mol. Catal., 16 (1982) 231.
6. Pouchert, C.J. "The Aldrich Library of infrared Spectra", 3rd ed. Aldrich Chem. Co. Ltd, Millwaukee, (1981).
7. Laine, R,M.; J. Mol, Catal., 14 (1982) 137.
8. Cotton, F.A.; and Wilkinson, G.; "Advanced Inorganic Chemistry", 5th ed., J.Wiley, (1988), P. 1057.
9. Foulds, G,A., J. Organometal. Chem., 296 (1985) 147.
10. Castinglioni, H., Giordano, R., and Sappa, E., J. Organ-ometal. chem., 362 (1989) 399.
11. Lau, C.P.; Ren, C.Y.; Chan, M.T. and Yang, C.H, J. Mol. Catal., 65 (1991) 287.
12. Shore, S.G., Organometallics, 5 (1986) 1041.
13. Pittman, C.U., in "Catalysis of Organic Reactions", ed. J.R. Kosak, Marcel Dekker, N.Y. (1984), P. 101.
14. Barrow, G.M., "Physical Chemistry," 5th ed., Mc Graw-Hill, Singapore (1984) P. 718.
15. a) Lappert, M.F. and Prolzai B.; Adv. Organometal. Chem., 5 (1967) 225.
    b) Wojcicki, A.; Adv. Organometal. Chem., 11 (1973) 88.
16. a) Halpern, J., Acc. Chem. Res., 15 (1982)
    b) Johnson, D.L. and Giladysz, J.A.; Inorg. Chem., 20 (1981) 2508.