Institute for Advanced Sustainability Studies (IASS)

# The Influence of Atmospheric Conditions on the Production of Ozone during VOC Oxidation

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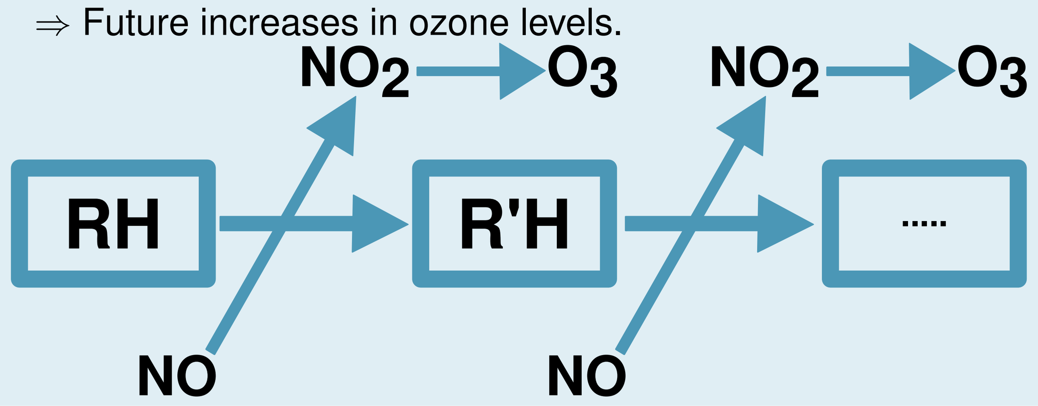
## Background

- Surface temperatures predicted to increase due to climate change.
- What are the effects of increased temperatures on air quality?
  - Increased emissions from vegetation (BVOCs).
  - Increased reaction rates atmospheric chemistry.
  - …
- Ozone is produced from the photochemistry of emitted $NO_x$ and VOC, with VOC being the "fuel" and $NO_x$ the "catalyst" for ozone production.
- Due to the photochemical nature of ozone production, meteorological factors such as temperature are drivers for ozone production.
- What are the effects of increased temperatures on tropospheric ozone concentrations?
  - Increased VOC emissions, especially BVOCs such as isoprene, are well-known to produce large amounts of ozone per molecule of VOC emitted.
  - Increased temperatures means that the PAN sink for peroxy radicals and $NO_2$ is much less-effective at transporting RO2 and $NO_2$ away from emission sources due to increased thermal decomposition rates.

⇒ Future increases in ozone levels.




## Motivation

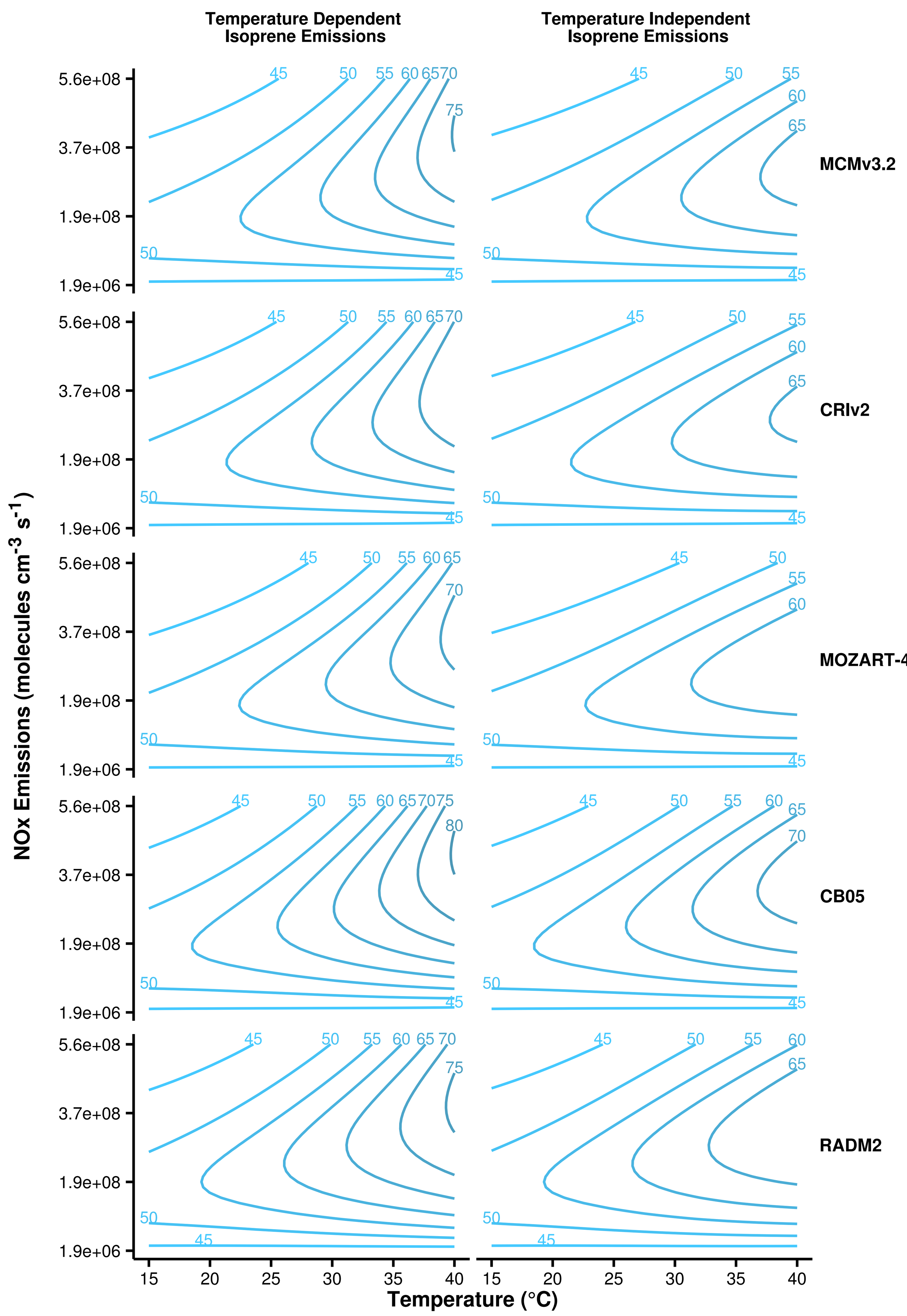
- Ozone levels over central europe are known to be driver by temperature. i.e. increases in temperature correlate with increases in ozone.
- Also confirmed in many studies over western and eastern US.
- This correlation is shown in many observational studies but modelling studies have tended to focus on the effects of increasing temperature on ozone under specific atmospheric conditions.
- How would changing NOx emissions influence the ozone produced with increases in BVOC and chemistry?
- Are increased BVOC emissions or increased chemistry more dominant?

## Approach

- Idealised box model simulating central europe (Benelux).
- Systematic variations in NOx over temperature range (15 – 40 °C).
- Simulations repeated using temperature dependent and independent source of isoprene emissions.
- All simulations repeated using chemical mechanisms that represent atmospheric chemistry at different scales: Point - MCMv3.2; regional - CRIv2, RADM2, CB05; global - MOZART-4.

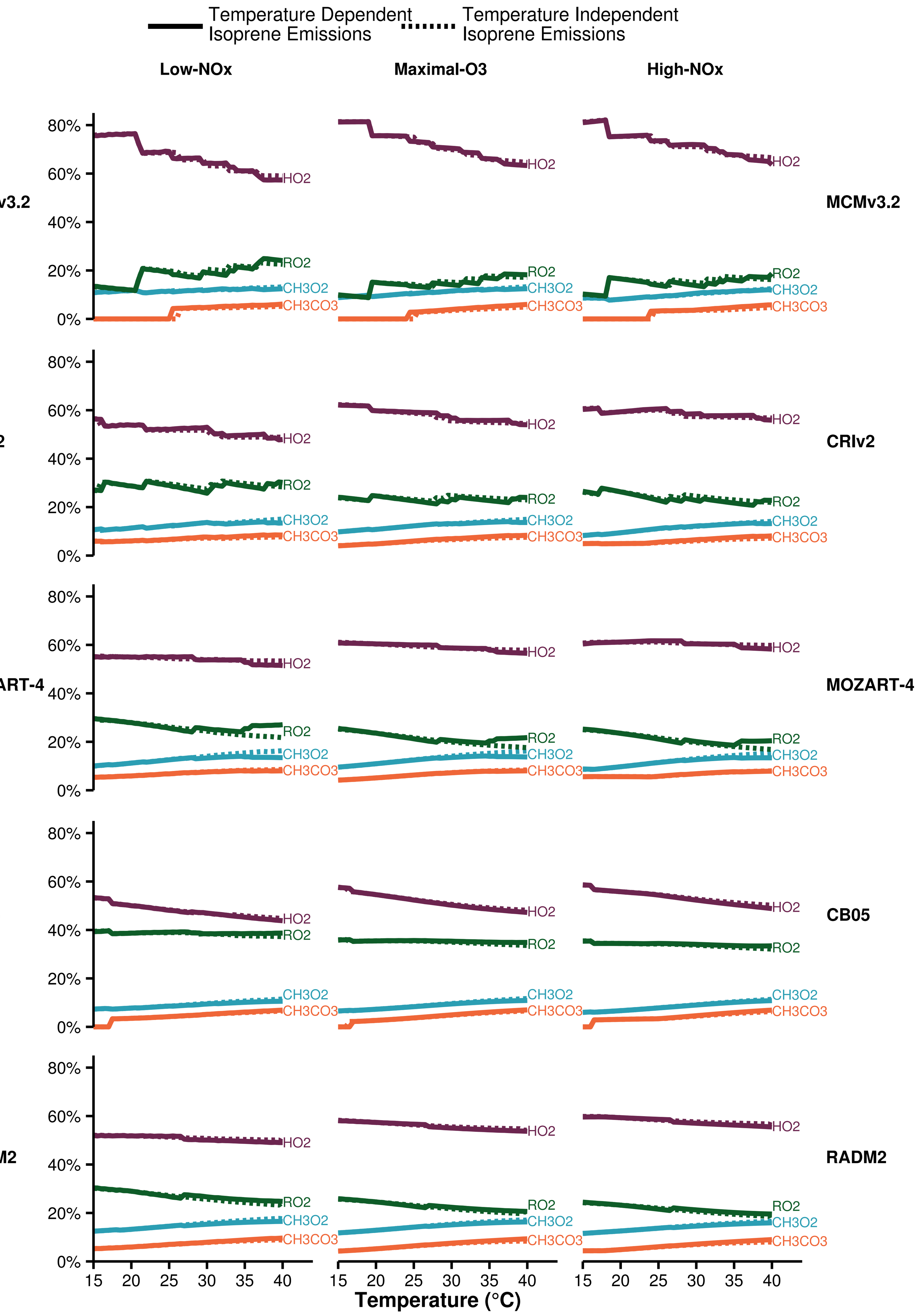
## Results

### Ozone Mixing Ratios in ppbv as a Function of NOx and Temperature




- Non-linear relationship of ozone mixing ratios with $NO_x$ and temperature, reproduced by all chemical mechanisms.
- Higher ozone produced using RADM2 and CB05 compared to detailed chemistry of MCMv3.2.
- Increased ozone when including temperature dependent source of isoprene, especially at high-$NO_x$.
- Lower $NO_x$ levels have lowest ozone mixing ratios with both temperature dependent and independent source of isoprene.

### Contributions of Peroxy Radical + NO Reaction to $O_3$ Budgets




- Assigned the ozone produced to three $NO_x$-regimes based on $H_2O_2/HNO_3$.
- The contributions of the reactions of peroxy radicals with NO to $O_x$ (= $O_3 + NO_2$) production budgets are determined for each $NO_x$-condition.
- Contributions of methyl peroxy ($CH_3O_2$) and acyl peroxy ($CH_3CO_3$) to $O_x$ budget increases with temperature.
- $CH_3CO_3$ is a precursor of $CH_3O_2$ which in turn is a precursor of $HO_2$. Thus increased source of a precursor of $CH_3CO_3$ - acetaldehyde - leads to higher ozone production.
- Acetaldehyde is an important carbonyl product, especially during isoprene

## Conclusions

- Lower NOx levels produces the least amount of ozone regardless of the increases of emissions and chemistry. Thus, target decreases in $NO_x$ emissions.
- All chemical mechanisms reproduce the non-linear relationship of ozone on $NO_x$ and temperature.
- CB05 and RADM2 over-estimate the increases of ozone with temperature compared to detailed chemistry of MCMv3.2.
- The treatment of secondary chemistry in CB05 and RADM2 promotes ozone production through more aldehyde production at the expense of ketones which leads to increased levels of acyl peroxy radical ($CH_3CO_3$). The further degradation on $CH_3CO_3$ produces more ozone.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